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Electron Paramagnetic Resonance Characterization and Thermal Decay of Radicals Trapped in a Photopolymerized Triacrylate Monomer

Elena Selli,* Cesare Oliva and Alberto Giussani
Dipartimento di Chimica Fisica ed Elettrochimica e Centro C.N.R., Università di Milano, via Golgi 19, I 20133 Milano, Italy

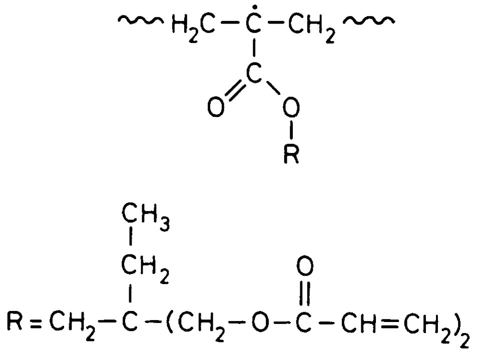
Radicals trapped during the photopolymerization and photo-cross-linking of 2-ethyl-2-hydroxymethylpropane-1,3-diol triacrylic ester have been studied by EPR spectroscopy at different temperatures (25–180 °C) and their thermal decay has been followed at 120 °C and 150 °C. Performing a fitting procedure on the EPR signals showed that they are composed of two kinds of patterns, which superimpose with the same g value. One of them is a single-line spectrum, while the other is hyperfine-structured. An exchange between two radical conformations is revealed by the latter, with the rate depending both on temperature and on the molar fraction of radicals giving the single-line spectrum. This suggests that both species are involved in the exchange mechanism. Termination occurs preferentially between radicals giving the same EPR pattern. Second-order termination rate constants depend on the photoinitiator concentration in the irradiated photoreactive mixture and give information about the microstructure of the polymer.

It is well known[1,2] that the formation of a network and the subsequent vitrification which accompanies the photoinduced polymerization and cross-linking of multifunctional monomers progressively inhibit the diffusion of reactive groups towards chain-propagating radicals. Consequently radical species are trapped within the polymeric matrix and all the rate constants are dependent on conversion.

The presence of extremely long-lived radicals trapped in pre-irradiated multifunctional acrylates has already been evidenced by EPR spectroscopy.[3–5] At room temperature very similar EPR spectra have been reported for different multiacrylate monomers.

Our previous investigations concerned the interpretation of the EPR spectra obtained with diacrylate monomers irradiated in various experimental conditions, as well as during radical decay at different temperatures up to 120 °C.[6–9] Identical spectra were observed under UV irradiation *in situ* and post-irradiation. They were fitted by an automatic non-linear least-squares procedure and turned out to be the superimposition of a three-line and a single-line pattern, both due to the same radical species. This was not the propagation radical, but a mid-chain radical, resulting from tertiary hydrogen abstraction from the polymer chain (see Scheme 1). The hyperfine interaction was removed in the single-line EPR pattern by electron spin–spin exchange between radicals surrounded by a more rigid, cross-linked environment.

The whole EPR spectral shape was dependent on the characteristics of the polymer structure. In fact different ratios between the integrated area of single-line and three-line EPR patterns were measured,[8] when different amounts of photoinitiating species were added to diacrylate monomers. This was attributed to the different average polymer chain lengths produced after UV irradiation, also influencing the rate of both radical trapping and radical decay.


(TA)

Scheme 1

In the present work we extend our study to radicals trapped in an even more cross-linked polymer structure, *i.e.* radicals produced during the photopolymerization and photo-cross-linking of a triacrylate monomer, 2-ethyl-2-hydroxymethyl-1,3-propanediyl triacrylate (TA). These radicals turned out to be rather stable up to temperatures as high as 180 °C. Consequently a systematic study of the EPR spectral shape could be carried out at a range of higher temperatures, thus evidencing phenomena which could not be observed at lower temperatures with radicals trapped in irradiated diacrylates.

Experimental

Materials

2-Ethyl-2-hydroxymethylpropane-1,3-diol triacrylic ester (TA)[2-ethyl-2-(1-oxoprop-2-enyloxymethyl)propane-1,3-diyl diacrylate, $EtC(CH_2OCOCH{=}CH_2)_3$] was purchased from BASF, Germany. It was washed with sodium hydroxide 2 mol dm^{-3} and then several times with saturated NaCl aqueous solutions. It was successively dried over anhydrous sodium sulfate and molecular sieves 4A (Union Carbide, USA) and then stored at 4 °C in darkness.

The photoinitiator, 2,2-dimethoxy-1,2-diphenylethanone, from BASF, Germany, was used as received.

Sample Preparation

Monomer, either pure or mixed with photinitiator (0.6–3.0 wt.%), was sealed under vacuum in a quartz EPR tube and then irradiated with UV–VIS light for 12 min outside the spectrometer cavity. The previously described apparatus and experimental procedure were employed.[6,7]

Analysis of residual unsaturations was carried out by IR spectroscopy, as already described.[7] The peak at 812 cm^{-1} corresponding to the $CH_2{=}CH{-}$ twisting vibration of the acrylate group[10] was used. This revealed that after the same

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standard irradiation time (12 min) the samples irradiated in the absence of the photoinitiator reached a conversion degree of acrylate groups of 20%, while in the presence of the photoinitiator *ca.* 70% of the initial acrylate functions have disappeared.

EPR Spectroscopy and Fitting Procedure

EPR spectra were recorded by means of a Varian E-line Century Series EPR spectrometer equipped with a laboratory-built variable-temperature facility. The sample temperature was kept at the desired value ±1 °C. EPR measurements were started within 15 min after the end of irradiation. Samples pre-irradiated in the presence of the photoinitiator showed an EPR signal of *ca.* ten-fold greater intensity than samples of pure monomer.

Digitized spectra were transferred to a Convex C120 computer, in order to fit them using the program EPR85.[11] A model based on Lorentzian spectral shapes always gave better fits than Gaussian line shapes. The least-squares fitting procedure yielded the width, eventual hyperfine splitting, *g*-factor and spectral area of each overlapping pattern. The statistical error affecting each parameter was also obtained. The quoted hyperfine parameters were the mean values calculated from all recorded EPR spectra. Their accuracy was at least 0.2 G. Furthermore, the employed fitting procedure allowed an evaluation of the rate constants of the dynamical processes affecting the EPR pattern.

Radical decay kinetics were followed by monitoring the EPR intensity at various temperatures. Radical concentration was assumed to be proportional to the numerical integrated area of the corresponding EPR pattern. In order to express rate constants in concentration units, rather than in arbitrary units deriving from the integration of spectral areas, the absolute radical concentration was roughly calibrated under the same registration conditions by means of a Varian strong pitch. The radical concentration was around 10^{-2} mol dm^{-3} in samples irradiated in the presence of photoinitiator.

Results

EPR Spectra at Different Temperatures

Samples irradiated in the absence of photinitiator were characterized by a much lower conversion degree of acrylate bonds and by a lower content of radicals. Less reliable results were obtained from the corresponding low-intensity EPR spectra. However, we were able to establish that they changed with temperature and with time in a way similar to EPR spectra recorded with samples obtained in the presence of photoinitiator.

Experimental EPR spectra recorded in the temperature range 25–170 °C in the presence of 1% photoinitiator are reported in Fig. 1. At the lower temperatures [Fig. 1(*a*)–(*d*)] they are very similar to the ones detected with the previously investigated pre-irradiated diacrylates at the same temperatures. In fact they can be very well fitted assuming the previously proposed model[6–8] of a three-line pattern, with a hyperfine coupling constant $a_{2H} \approx 26$ G, overlapping a single-line spectrum. The former can be attributed to a radical species R$^\bullet$ in a rather mobile environment, the latter to the same radical species, labelled in this case by S$^\bullet$ to mind that its environment is essentially solid.

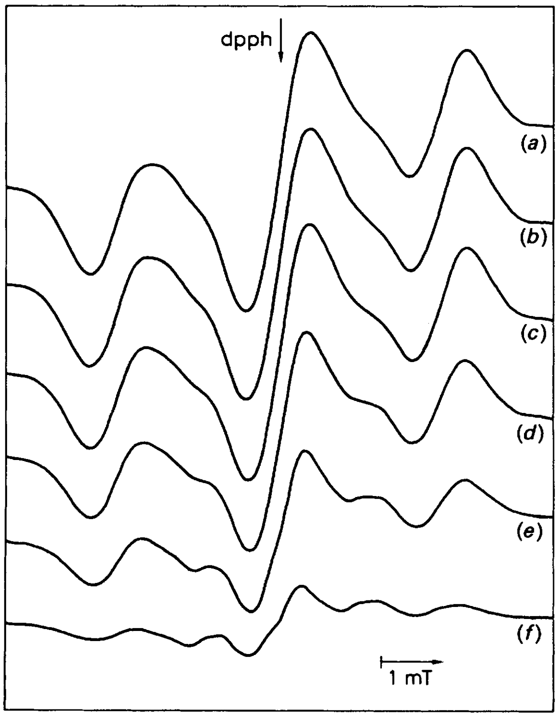

Fig. 1 EPR spectra at different temperatures of TA pre-irradiated in the presence of 1% photoinitiator. (*a*) 25; (*b*) 50; (*c*) 80; (*d*) 110; (*e*) 140; (*f*) 170 °C.

At higher temperatures, however, two new EPR lines appear in between the central line and the side ones [Fig. 1(*e*)–(*f*)], narrowing and increasing with temperature. These lines had never been observed with irradiated diacrylates in previous studies.[3–8] However, note that the EPR spectrum of these systems had never been recorded at such a high temperature. The proposed model[6–8] of interpretation of EPR spectra had therefore to be modified in order to take into account this new experimental evidence (see Discussion).

Radical Decay Kinetics

Highly cross-linked networks are obtained by photopolymerizing the trifunctional monomer in the presence of photoinitiator. Owing to the very entangled polymer structure, radical decay could be observed at a reasonable rate only at temperatures higher than 100 °C. Consequently, radical decay kinetics have been studied at 120 °C and 150 °C in polymeric systems obtained both in the absence and in the presence of different amounts of photoinitiator.

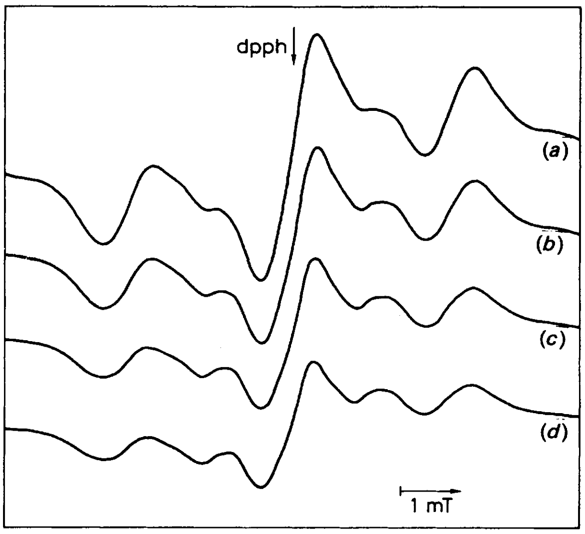

Fig. 2 EPR spectra of TA pre-irradiated in the presence of 0.6% photoinitiator at various times during radical decay kinetics at 120 °C. (*a*) 24; (*b*) 107; (*c*) 287; (*d*) 463 min.

Fig. 2 shows a series of EPR spectra recorded at various

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times during radical decay at 120 °C. The two 'new lines' appear to become more intense and well defined in the course of each kinetic run. So the EPR spectrum is similar to the already reported[3–8] spectrum of diacrylates only at the beginning of radical decay, whilst this more complex hyperfine structure emerges during radical decay and parallel increase of double bonds conversion.[6,9] Consequently variation of temperature and radical decay time seem to produce the same spectral variation.

Discussion

The radical structure which originates the three-line EPR spectrum typical of radicals trapped in multifunctional acrylates has been unequivocally identified[12] as a mid-chain radical surrounded by four β-methylene protons reported in Scheme 1. The R group has the structure indicated in the scheme, if the monomer is TA, as in the present work. Of course the whole polymer structure is not linear, as the pendant acrylate functions are able to react further, giving cross-linking.

The fact that only two of the four β-methylene protons of the mid-chain radical of Scheme 1 show appreciable hyperfine interaction has recently been attributed[13] to the conformation of the CH_2 groups adjacent to the mid-chain polyacrylate radical. This conformation should be offset (±10°) from a symmetric arrangement where the two protons would both have a dihedral angle of 60°. However, a good match between experimental and simulated EPR traces was obtained[13] only if a Gaussian distribution of conformations was assumed, spread around the most probable dihedral angle. Two different energy minima, on the contrary, have been hypothesized elsewhere for radicals trapped in methacrylates,[14] corresponding to two orientations of the CH_2 groups with respect to the C_α—C_β bond.

Exchange between Radical Conformations

Dependence on Temperature

An exchange between two conformations $R_1^{\bullet}$ and $R_2^{\bullet}$ can be hypothesized by us in the present case at least at the higher temperatures, so that the two couples of β-methylene protons can exchange with each other. This exchange would be rather slow at temperatures up to 100 °C, as the expected five lines broaden and collapse into only three lines. At higher temperatures, on the contrary, the exchange would become fast, as all the five lines emerge in the EPR spectrum (Fig. 1). In any case, the single-line spectrum overlapping the abovementioned EPR pattern results from a washing-out of the hyperfine structure due to a strong spin–spin exchange occurring between radical species $S^{\bullet}$ surrounded by more cross-linked regions, as in the model already proposed for diacrylates.[6–8]

Good fittings of the experimental EPR spectra at different temperatures have been obtained according to this interpretation (see Fig. 3). A hyperfine coupling constant $a_{4H} = 13.0 \pm 0.2$ G and a linewidth $\Delta W_1 = 6.9 \pm 0.2$ G have been calculated for the structured pattern, while $\Delta W_2 = 9.3 \pm 0.2$ G for the single-line pattern. The linewidth narrowing observed at higher temperatures in the former spectrum evidences the increase in the exchange speed between two conformations of four protons, divided into two groups of completely equivalent protons. The exchange time, τ/s, has been evaluated according to the following equation:[15]

$$\Delta W_{\text{exch}} = \frac{|\gamma_e|}{2\sqrt{3}}(a_{\text{I}} - a_{\text{II}})^2\tau \qquad (1)$$

ΔW_{exch} (G) is the exchange contribution to the width of the EPR lines characterized by a total nuclear spin quantum number $m_z = \pm 1$; $|\gamma_e| = 17.61 \times 10^6\ \text{s}^{-1}\ \text{G}^{-1}$ is the magnetogyric ratio, a_{I} and a_{II} (G) are the hyperfine coupling constants of the two couples of protons involved in the exchange process. We have assumed $a_{\text{I}} = 21$ G and $a_{\text{II}} = 6$ G, following the calculations reported in ref. 13.

The τ value decreases from 14.1 ± 0.6 ns at 25 °C to 3.1 ± 0.1 ns at 170 °C in a sample pre-irradiated in the presence of 1% photoinitiator. Somewhat lower values have been calculated in a less cross-linked polymer structure obtained by irradiating the monomer in the absence of the photoinitiator (13.4 ± 0.4 and 2.5 ± 0.3 ns at 25 and 180 °C, respectively). However, τ values do not decrease with tem-

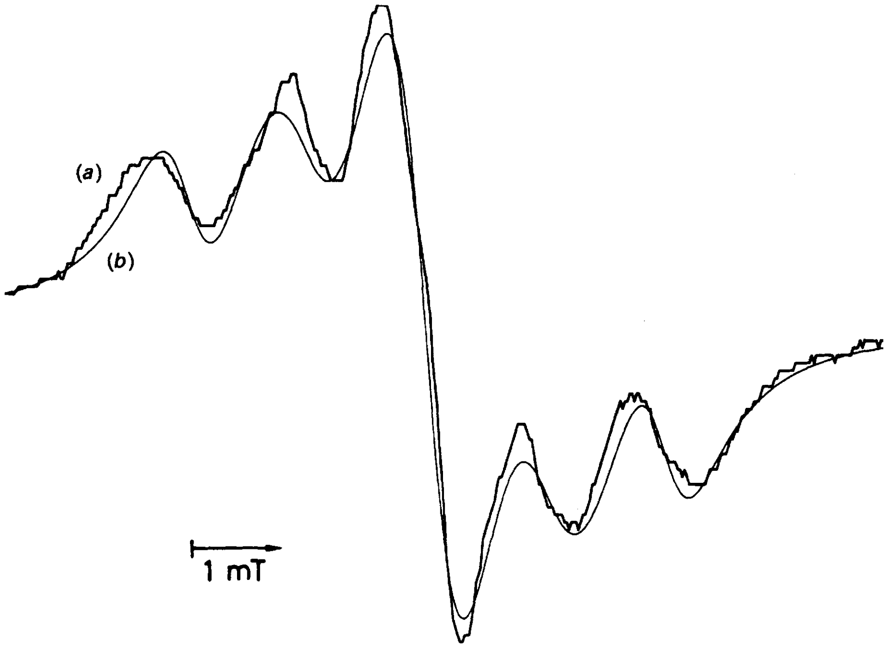

Fig. 3 EPR spectrum of pre-irradiated TA (1% photoinitiator) recorded after 61 min at 150 °C. Line (*a*) experimental spectrum; line (*b*) least-squares computer synthesized spectrum.

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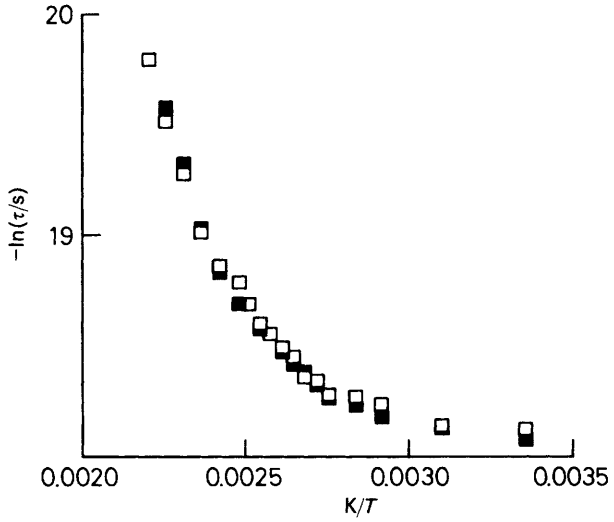

Fig. 4 $-\ln(\tau/s)$ *vs.* T^{-1} for TA photopolymerized (□) without photoinitiator or (■) in the presence of 1% photoinitiator

perature according to an Arrhenius plot (see Fig. 4), as the exchange activation energy increases continuously with increasing temperature, being *ca.* 2.3 kJ mol^{-1} at room temperature and *ca.* 9.6 kJ mol^{-1} at 150–180 °C, while the pre-exponential factor also increases by five orders of magnitude. These effects are clearly the consequence of the great modifications occurring in the polymer structure with increasing temperature.

Dependence on Composition

The fitting of EPR spectra recorded successively in radical decay kinetic runs evidences the fact that the exchange rate increases with time. Also, the molar fraction of radicals $S^{\bullet}$ giving a single-line spectrum increases continuously with decay time, ranging from 0.18 to 0.34 under the different experimental conditions. This further confirms the attribution of this type of spectrum to radicals present in a more rigid structure, as during each kinetic run of radical decay further polymerization and cross-linking occur in the dark.

Fig. 5 shows how the exchange time correlates also with the molar fraction $x(S^{\bullet})$ and so also with the degree of polymerization and cross-linking of the polymer sample. The following empirical equation fits the experimental data:

$$\tau = \tau_0 - \kappa x(S^{\bullet}) \qquad (2)$$

Nearly the same slope $\kappa = 37$ ns can be calculated for all the photoinitiator contents, while τ_0 varies from 12 ns to 16 ns. A slightly higher exchange rate, at the same value of $x(S^{\bullet})$, is noticed at a lower percentage of the photoinitiator. When both $x(S^{\bullet})$ and percentage of photoinitiator are the same, a faster exchange is observed, as expected, at higher temperatures.

So the rate of exchange of the two couples of β-methylene protons depend in general on the microstructure of the polymer. In particular, the fact that the exchange rate is so essentially dependent on the molar fraction of radicals $S^{\bullet}$ indicates that the exchange is not only an intramolecular process taking place within the two conformations $R_1^{\bullet}$ and $R_2^{\bullet}$, but it must also have an intermolecular component involving $S^{\bullet}$ species, according to the following equation:

$$R_1^{\bullet} + S^{\bullet} \rightleftarrows R_2^{\bullet} + S^{\bullet} \qquad (3)$$

This reaction is fast (*ca.* 10^{-8} s) on the EPR scale.

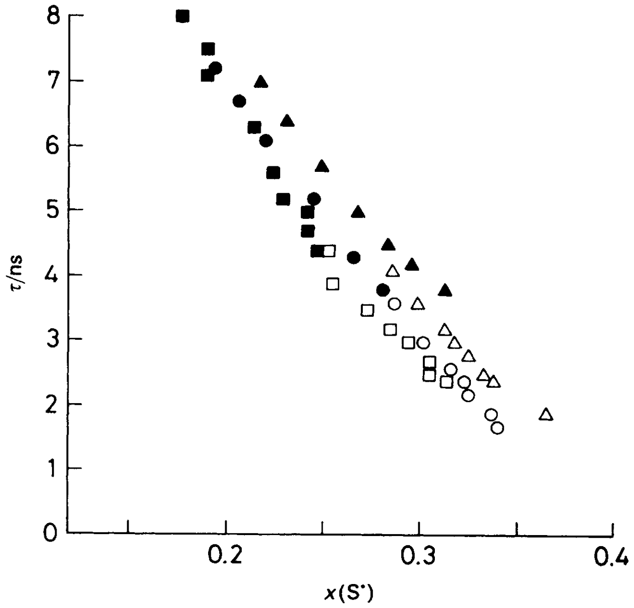

Fig. 5 Exchange time between radical conformations $R_1^{\bullet}$ and $R_2^{\bullet}$, τ *vs.* molar fraction $x(S^{\bullet})$. Data have been calculated from EPR spectra recorded during radical decay kinetic runs at 120 °C (solid symbols) and 150 °C (open symbols). Amount of photoinitiator (■, □) 0.6%; (●, ○) 1.0%; (▲, △) 3.0%.

Radical Decay Kinetics

Both single-line spectra (due to $S^{\bullet}$) and EPR spectra with hyperfine structure (due to $R_1^{\bullet}$ and $R_2^{\bullet}$) decay with time at temperatures greater than 100 °C.

According to the classical termination mechanism, radicals should mutually terminate through recombination or disproportionation reactions, *i.e.* through bimolecular reactions. Radical decay can thus be interpreted in the light of the following kinetic scheme:

$$R^{\bullet} + R^{\bullet} \rightarrow \text{polymer} \qquad (I)$$

$$S^{\bullet} + S^{\bullet} \rightarrow \text{polymer} \qquad (II)$$

$$R^{\bullet} + S^{\bullet} \rightarrow \text{polymer} \qquad (III)$$

The mixture of radical conformations $R_1^{\bullet}$ and $R_2^{\bullet}$, giving the structured EPR spectrum, is indicated here by $R^{\bullet}$.

The following rate equations can thus be written:

$$-\frac{d[R^{\bullet}]}{dt} = k_R[R^{\bullet}]^2 + k_{RS}[R^{\bullet}][S^{\bullet}] \qquad (4)$$

$$-\frac{d[S^{\bullet}]}{dt} = k_S[S^{\bullet}]^2 + k_{RS}[R^{\bullet}][S^{\bullet}] \qquad (5)$$

These equations cannot be simply integrated. The evaluation of the three rate constants could only be obtained by an iterative calculation based on numerical integration methods. This procedure leads to reliable results only if a large amount of experimental data is taken into account. Moreover, in the present system radical concentrations $[R^{\bullet}]$ and $[S^{\bullet}]$ have values quite close to each other throughout every kinetic run, so that the two terms on the right of eqn. (4) and (5) cannot be easily distinguished.

However, we can reasonably assume that the encounter and termination involving two radicals trapped in different polymeric phases is less probable than termination between radicals belonging to the same phase. This means that $k_{RS}[R^{\bullet}][S^{\bullet}]$ should be smaller than $k_R[R^{\bullet}]^2$ and $k_S[S^{\bullet}]^2$ in

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Table 1 Termination rate constants at 120 °C and 150 °C in TA pre-irradiated in the presence of I (wt.%) of photoinitiator. k_R refers to radicals $R^{\bullet}$ giving EPR spectra with hyperfine structure and k_S to radicals $S^{\bullet}$ giving single-line spectra

I	$k_R/10^{-3}$ dm^3 mol^{-1} s^{-1}	$k_S/10^{-3}$ dm^3 mol^{-1} s^{-1}
120 °C		
0	5.4 ± 0.2	9.4 ± 0.4
0.6	0.84 ± 0.05	1.77 ± 0.06
1.0	0.87 ± 0.05	1.58 ± 0.05
3.0	1.58 ± 0.06	2.5 ± 0.1
150 °C		
0	39 ± 4	58 ± 4
0.6	14.9 ± 0.3	27.6 ± 0.2
1.0	12.9 ± 0.6	23.1 ± 0.7
3.0	15.7 ± 0.3	25.9 ± 0.6

eqn. (4) and (5), respectively. An indirect confirmation of this assumption is that the ratio:

$$\left\{\left(-\frac{d[R^{\bullet}]}{dt}\right)\Big/\left(-\frac{d[S^{\bullet}]}{dt}\right)\right\}\cdot\frac{[R^{\bullet}]^2}{[S^{\bullet}]^2}=\frac{k_R+k_{RS}([S^{\bullet}]/[R^{\bullet}])}{k_S+k_{RS}([R^{\bullet}]/[S^{\bullet}])}$$

oscillates randomly around an average value in the course of each kinetic run, while the ratio $[S^{\bullet}]/[R^{\bullet}]$ increases with decay time. Consequently k_{RS} should be small compared to k_R and k_S. The approach of two radicals $R^{\bullet}$ and $S^{\bullet}$ would simply produce the intermolecular exchange effect described by eqn. (3).

Within this assumption, the second-order rate constants k_R and k_S reported in Table 1 could be easily calculated as the slope of $[R^{\bullet}]^{-1}$ and $[S^{\bullet}]^{-1}$ *vs.* time plots. Straight lines have always been obtained, confirming the bimolecular termination mechanism.

A first-order decay of radicals trapped in pre-irradiated diacrylates was observed at lower temperatures by ourselves[6–8] and by other authors.[4,5] However, in the photopolymerization mechanism of multifunctional monomers both propagation and termination rate constants change during polymerization and cross-linking in darkness, as a consequence of a continuous reduction in mobility of the reacting medium.[16] Consequently only average apparent rate constants can be obtained when this effect is very strong.

In this study the higher attainable temperatures allow the polymeric system to gain enough mobility so that radical termination takes place according to the classical bimolecular mechanism. However, a small decrease in slope (*i.e.* in termination rate constant) of the reciprocal radical concentration *vs.* time plots has sometimes been noticed at the end of kinetic runs, due to a substantial increase in the rigidity of the medium.

The rate constants reported in Table 1 give some interesting information about the microstructure of the polymer networks obtained under different experimental conditions.

First of all, radical decay is much faster in samples photopolymerized in the absence of photoinitiator. The polymer matrix maintains in this case a higher mobility, as a consequence of the much lower conversion degree of acrylate double bonds reached during irradiation. A temperature increase is less effective, in this case, in producing any further enhancement of mobility.

As to the influence of the amount of photoinitiator mixed with the triacrylate monomer prior to irradiation, two opposite effects should be taken into account. It is well known, in fact, that in the presence of photoinitiators a greater amount of radical fragments are produced upon irradiation, which can simultaneously initiate a larger number of polymer chains. High double-bond conversions can thus be reached upon irradiation, leading to a much more cross-linked polymer, containing a greater amount of trapped radicals. However, by increasing the amount of photoinitiator, the concentration of radicals produced upon irradiation is also increased. Under these conditions both radical–radical and photoinitiator fragments–radical encounters are strongly favoured, thus reducing the average chain-length and cross-linking degree of the polymer. Consequently, an optimum photoinitiator content allows a maximum polymerization and cross-linking level to be reached for each polymeric system.

In the present case this seems to be obtained with a photoinitiator concentration equal to 1 wt.%, as radical decay rate constants k_R and k_S are higher at both lower (0.6%) and higher (3%) photoinitiator contents, clearly reflecting in both cases a higher polymer mobility.

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