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Electron paramagnetic resonance study of free-radical kinetics in ultraviolet-light cured dimethacrylate copolymers

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A spin-trapping technique and direct kinetic measurements of electron paramagnetic resonance spectra were used to investigate the kinetics of radical production in the cross-linking photo-initiator system based on camphoroquinone and dimethyl-aminoethylmethacrylate in the presence of the corresponding monomer dimethacrylate copolymer mixture, as well as in the pure photo-initiator system. Consequently, in both cases, the kinetics of radical production and decay was measured. From the measured data the formal kinetic parameters of particular radical processes were calculated by the non-linear least-squares regression method. © *1998 Chapman & Hall*

1. Introduction

The morphogenesis of a tetrafunctional network formed by radical polymerization of dimethacrylate monomers exhibits a number of interesting and not well-understood features resulting in several morphological peculiarities, which are not commonly observed in less functional networks, or networks produced by other types of polymerization process [1]. Commonly utilized dental filling composites are mostly based on rapidly curing mixtures of dimethacrylate monomers such as 2,2-*bis*[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane (*bis*-GMA) and triethyleneglycol dimethacrylate (TEGDMA) [2]. These monomers form, after a proper initiation, a three-dimensional tetrafunctional network by radical polymerization of methacrylate C=C double bonds [3–6]. Reactivity of methacrylate groups of both co-monomers is principally the same, resulting in the formation of a copolymer network with more or less random relative position of the co-monomers.

In this paper, we report kinetic parameters of radical processes occurring in studied dental polymer networks. The networks investigated were formed by a radical copolymerization of mixtures of *bis*-GMA and TEGDMA using a camphoroquinone mixed with dimethyl-aminoethylmethacrylate as the photo-initiator system. Because of the above mentioned radical nature of the polymerization process [4], electron paramagnetic resonance (EPR) was employed to measure quantitatively the kinetic parameters of radical production in the system, both in the initiator and in the bifunctional acrylate monomer mixture. In both cases, the kinetics of radical decay were measured and formal kinetic parameters of the radical decay were calculated.

2 Materials and methods

2.1. Chemicals

Bisphenol-A-*bis*(hydroxypropylmethacrylate) (*bis*-GMA) (lot no. 473416), urethanedimethacrylate (UDMA) (lot no. 141 9846), dodecanedioldimethacrylate (DDMA) (lot no. 411 291), triethyleneglycol-dimethacrylate (TEGDMA) (lot no. 407 666) were used (Rohm and Haas, USA). As a reference, the kinetics of ultraviolet-light stimulated radical production and decay for DDMA and TEGDMA were measured. To study the effect of the monomer viscosity and molecular mobility, two different samples were prepared by mixing various methacrylate monomers. Sample 1 was prepared by mixing 43 wt % *bis*-GMA

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with 14 wt% UDMA and 41 wt% DDMA. Sample 2 was prepared by mixing 34 wt% *bis*-GMA with 28 wt% UDMA and 38 wt% TEGDMA.

Camphoroquinone (CPQ) (lot no. 14967) (AVOCADO-Research Chemicals, 99%) has been used as the photoinitiator and dimethyl-aminoethylmethacrylate (DMAEM) (lot no. 28955/1) (Janssen Chimica, 98%) was used as the redox system.

For EPR spin-trapping experiments, a Nitrosodurene spin trap (Oklahoma Spin Trap Center) was used. Iso-propanol used in this study was purchased from Lachema Brno.

2.2. Electron paramagnetic resonance spectroscopy

A Bruker 200 D Spectrometer equipped with an Aspect 2000 Computer and the corresponding Bruker Standard Program was used to obtain and to analyse the EPR spectra. The corresponding solutions placed in quartz tube or a flat cell were irradiated directly in the cavity of an EPR spectrometer. The measurements were carried out at 295 K in air (for samples 1, 2, and DDMA, TGDMA) or under an argon atmosphere (for the investigations of initiator system consisting of camphoroquinone dissolved in dimethylaminoethylmethacrylate or iso-propanol), and additionally in the case of spin-trapping experiments, the studied solutions were saturated with nitrosodurene.

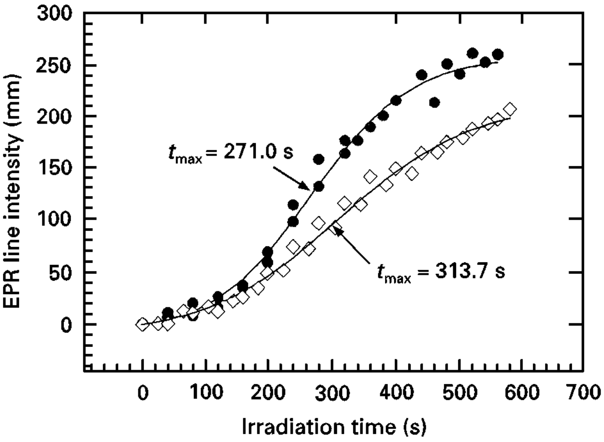

Figure 1 Kinetics of the production of photo-chemically generated radicals by the CPQ/DMAEM-initiating system in different dimethacrylate matrices in (◇) sample 1, (●) sample 2.

TABLE I Results of the least-squares non-linear regression of the kinetics of the photochemical production of radicals in CPQ-DMAEM initiating system in different dimethacrylate matrices as shown in Fig. 1

Sample	Model parameters			t_{MAX} (s)
	$k_{EPR}c_{0A}$ (mol^{-1})	$k_{EPR}c_{0P}$ (mol^{-1})	$k_{AUTOCAT}$ (10^5 mol s^{-1})	
1	215.3 ± 7.7	11.04 ± 2.5	4.184 ± 0.511	313.7
2	259.1 ± 6.1	7.6 ± 2.0	4.883 ± 0.489	271.0

2.3. Irradiation apparatus

For sample irradiation directly in the EPR spectrometer cavity, a medium-pressure mercury lamp ($\lambda \geqslant 300$ nm) (NARVA, Germany) was used.

2.4. Calculation of formal kinetic parameters

Kinetic data of the time dependence of gradual change of radical concentration during the irradiation of the initiator system in different monomer matrices, were treated using an hypothesis of an autocatalytic process (Fig. 1). It is known, that the radical production in such systems is accelerated by increasing the number of radicals produced in the system. The integrated form of the expression for the time-dependent changes of radical concentration, x, is as follows [7]

$$x = c_{0P}\frac{e^{at} - 1}{1 + be^{at}} \tag{1}$$

where $a = (c_{0A} + c_{0P})\, k_{AUTOCAT}$, $b = c_{0P}/c_{0A}$; c_{0A} is the starting concentration of the reactant, c_{0P} is the starting concentration of the product; $k_{AUTOCAT}$ is the rate constant of the autocatalytic reaction. We propose a linear relation between the EPR line intensity, I_{EPR}, and the corresponding radical concentration, $I_{EPR} = k_{EPR} * c_i$ (for results see Table I). The parameter t_{max} corresponds to the time at which the reaction rate is maximum.

From the measured EPR spectra, first-order kinetics parameters were calculated to characterize the rate of radical decay as a function of the matrix composition. Theoretical treatment of the observed radical decay data was divided into two separate processes (the fast process and the slow process) (see Fig. 2). Then, each process was treated as a first-order kinetic mechanism according to the formula [8]

$$c_i = c_{0i}e^{-k_1^j t} \tag{3}$$

where c_i is the concentration of the ith radical intermediate; c_{0i} is the corresponding starting concentration (at the time of the irradiation stop) of the ith radical intermediate; k_1^j is the first-order rate constant of the jth process (where $j = f$ or s, f – fast process, s – slow process). Corresponding radical half-times, $\tau_{1/2}^j$ were calculated as

$$\tau_{1/2}^j = \frac{\ln 2}{k_1^j} \tag{4}$$

The parameter t_{CRIT} corresponds to the calculated time of the cross-point of the fast and slow processes. Results of the non-linear least-squares regression of experimental data with the values of the first-order kinetic rate constants and of the corresponding half-times of the studied radical decay during cross-linking reactions, are given in Table II.

3. Results and discussion

One of the features of radical polymerization is its addition character, i.e. reaction proceeds via adding monomers to the growing polymer chains. The

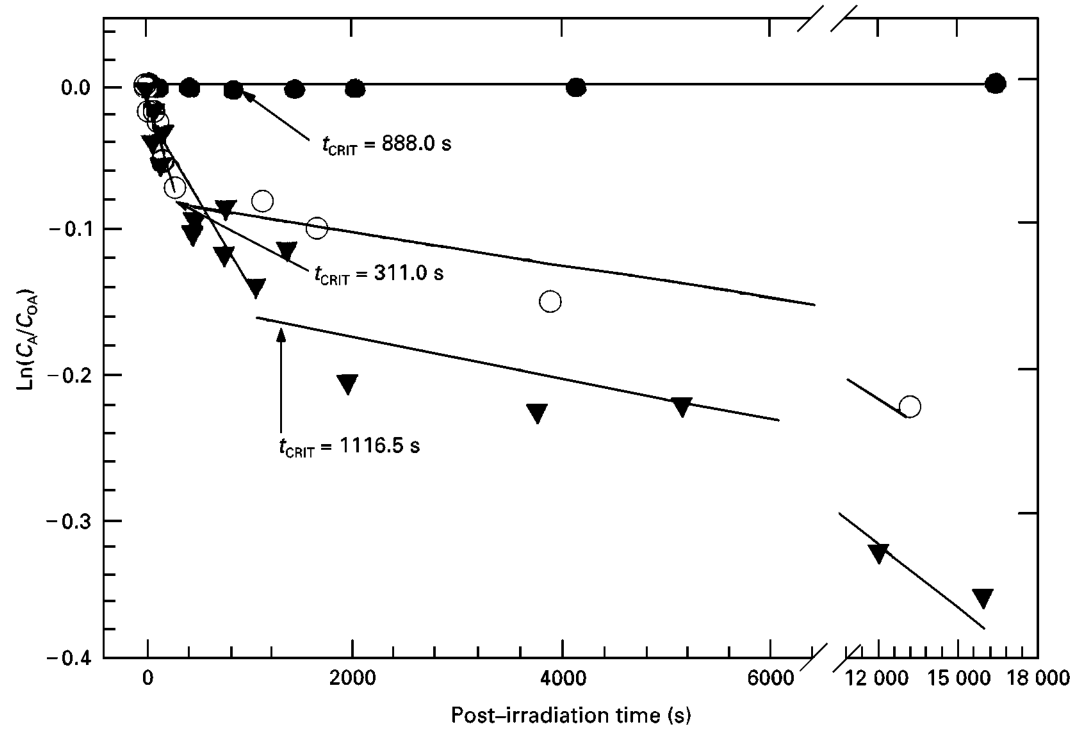

Figure 2 First-order kinetics plot of the radical decay (after ceasing of irradiation) of the CPQ/DMAEM photo-initiator system applied in different monomer matrices in (●) DDMA, (○) TEGDMA, and (▲) sample 2.

TABLE II Results of the least-squares non-linear regression of the data shown in Fig. 2

Sample	Fast process		Slow process		t_{CRIT} (s)
	k_1^f ($10^5\,s^{-1}$)	$\tau_{1/2}^f$ (h)	k_1^s ($10^5\,s^{-1}$)	$\tau_{1/2}^s$ (h)	
TEGDMA	26.243	0.733	1.151	16.722	311.0
DDMA	0.382	50.556	0.000	∞	888.0
1	36.357	0.531	0.017	1111.111	526.0
2	23.682	1.310	4.968	9.335	1116.5

reacting system always contains a high molecular weight polymer of a certain distribution of molecular weights and monomer species at the same time [8]. The kinetics of radical polymerization in cross-linked polymers are characteristic of the extremely low degree of conversion observed at a gel point [2]. For all our systems under study, T_g was above 313 K. Decreased mobility of growing radicals results in autocatalytic effects at low conversions, resulting in the presence of a relatively large number of "living" radicals in a completely cured system [5].

The relatively moderate degree of conversion achieved commonly in thermally cured dental polymers (typically 5%–70%) may be of concern for both material performance in an application and possible toxicity of unreacted leaching-out monomers. A somewhat higher degree of conversion of up to 85% is achieved for ultraviolet and visible light-cured unfilled dental resins used as sealants, adhesives, etc. [3].

Dušek [1] has suggested that the formation of a radically polymerized network can proceed in two steps. In a first step, microgellation occurs which is, in the second step, followed by connection of microgels, resulting in an inhomogeneous network morphology. Moreover, he has suggested that, depending on the molecular weight and flexibility, microgellation can be proceeded by cyclization at an oligomer level. It has been shown [2] that during a copolymerization of a linear methyl methacrylate (MMA) and ethyleneglycol dimethacrylate (EGDMA), linear PMMA chains are cross-linked by EGDMA linkages. However, only one-third of EGDMA formed cross-links [9]. For the remaining two-thirds of EGDMA monomer, only one methacrylate group of each EGDMA molecule entered the copolymerization reaction. Hence, about 30% of the total amount of C=C bonds remained unreacted in the form of pendant groups (PG). The amount of unreacted C=C bonds increases substantially in the case of copolymerization of two dimethacrylates such as *bis*-GMA and TEGDMA. It has been shown that the quantity of unreacted unsaturations in the *bis*-GMA/TEGDMA system can be qualitatively correlated with the amount of *bis*-GMA in the polymerizing system [10–12] and that neat TEGDMA exhibits about 10% higher degree of conversion than neat *bis*-GMA [10].

3.1. EPR investigations of the cross-linking photo-initiator system

The experimental EPR spectrum together with its simulation observed during the irradiation of the initiator system consisting from saturated ketone (camphoroquinone) dissolved in dimethyl-aminoethylmethacrylate solution is depicted in Fig. 3a. From its simulation, relatively low splitting consants ($4\,a_H = 0.055$ mT, $2\,a_H = 0.26$ mT and $a_H = 0.335$ mT) were extracted indicating that the unpaired electron is centred in the neighbourhood of the EPR silent atom.

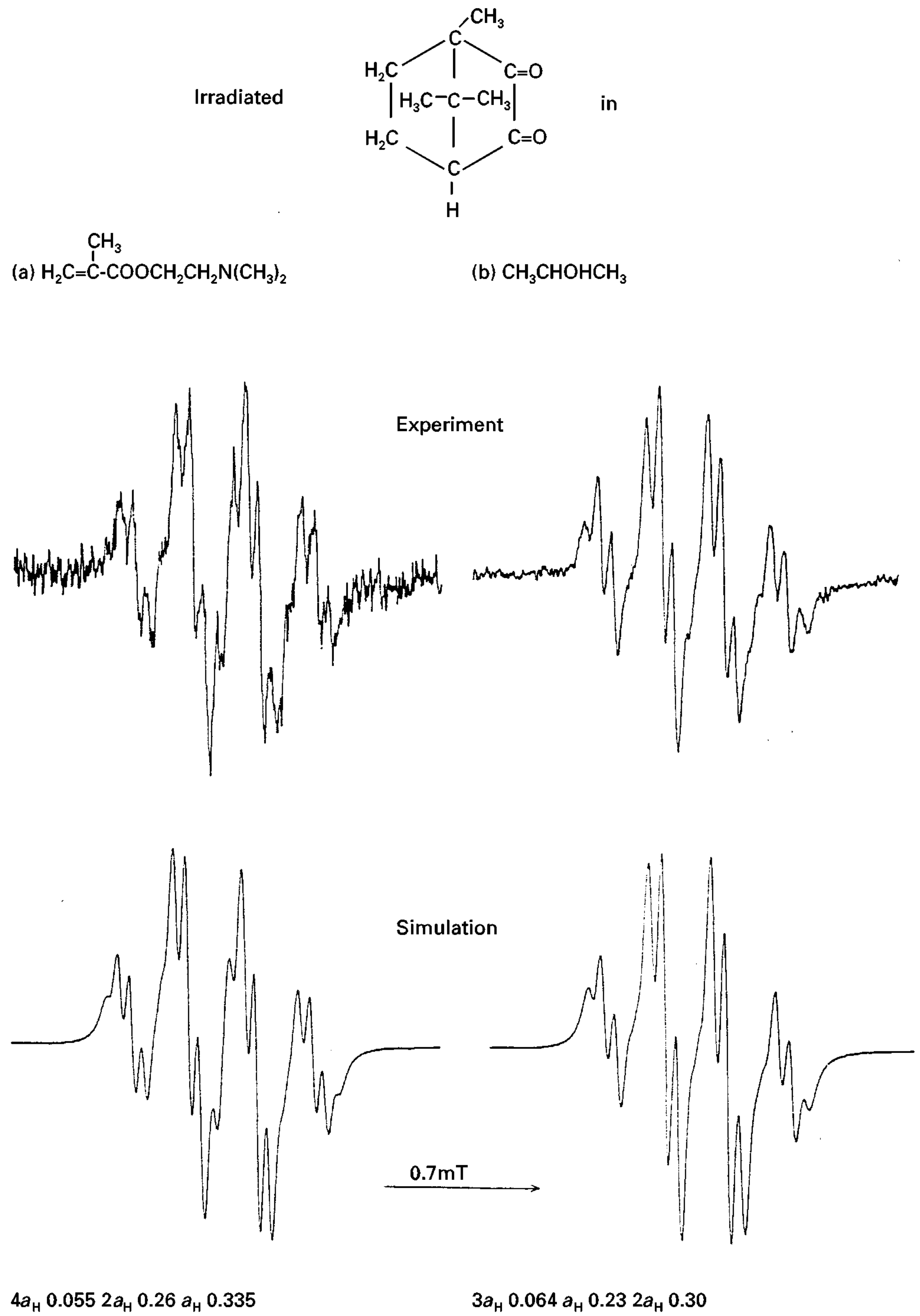

Figure 3 Experimental and simulated EPR spectra of CPQ photo-initiator system (splitting constants in mT) in (a) DMAEM, and (b) iso-propanol.

The carbonyl groups from acrylate or ketone were the potential positions for such an arrangement. The number of splitting constants favours the assumption, that the radical most probably originates from camphoroquinone (CPQ) and not from dimethylaminoethylmethacrylate (DMAEM). To confirm this assumption, we carried out an analogous experiment by replacing DMAEM solution (Fig. 1a) by isopropanol. The obtained EPR spectra were very similar (Fig. 3b) to the spectra observed in the CPQ/DMAEM solution. Similarly as in DMAEM solution, there is a group with a very low splitting constant ($3a_H = 0.064\,mT$) and a further group with higher splitting constants ($a_H = 0.23\,mT$ and $2a_H = 0.30\,mT$). This confirms that the radical formed does not decisively depend on the presence of DMAEM, consequently, it originates from CPQ.

An unambiguous determination of the exact radical structure with the spectra shown in Fig. 3 is not possible from the data available so far. Irradiated isopropanol solutions are known to donate hydrogen to the ketyl groups =CO under the formation of the carbon-centred radical $^{\bullet}$COH< . The ketyl group in position p1 with the distant methyl groups could be assigned to the spectrum observed, but the non-equivalence of the three protons with larger splittings

($a_H = 0.23\,\text{mT}$ and $2a_H = 0.30\,\text{mT}$ in Fig. 3b and $2a_H = 0.26\,\text{mT}$ and $a_H = 0.335\,\text{mT}$ in Fig. 3a), hypothetically assigned to one of the methyl groups, are not well understood, as methyl protons are usually equivalent at the room temperature. Additionally, the radical structure shown in Fig. 3a, formed in the presence of DMAEM, contributes to low splitting ($4a_H = 0.055\,\text{mT}$, e.g. adequate with one methyl group and a further proton), whereas the structure in Fig. 3b contributes only three equivalent protons ($3a_H = 0.064\,\text{mT}$ – most probably they originate from the methyl group). Therefore, a structural rearrangement of CPQ with some substitution reaction cannot be excluded.

Some further additional information on the radical formed was obtained using the nitrosodurene spin trap. The original radical with spectra presented in Fig. 4 are unstable, and decay immediately after stopping the irradiation with a half-time certainly shorter than 1 s, as extracted from the EPR measurements. (Our limited time resolution prevents a more exact half-time from being specified.) Consequently, the initiator system was irradiated (i.e. CPQ dissolved in DMAEM solution under an argon atmosphere) in the presence of a nitrosodurene spin trap. The time evolution of the spectra obtained is shown in Fig. 4. Even before the irradiation (at time $t = 0\,\text{s}$) a low but definite radical concentration was found by the first sweep (probably due to the irradiation of the initiator system with daylight), but the radical concentration increased considerably with progressing irradiation, as shown in Fig. 4. After about 5 min, a stationary concentration was established and on switching off the irradiation, the radical adduct decayed with a half-time of the order of several minutes. A characteristic experimental spectrum was simulated, as shown in the inset of Fig. 4. Two spin adducts are evident, one with splitting constants $a_N = 1.34\,\text{mT}$ and $a_H = 2.13\,\text{mT}$. This radical is present in low concentration from the beginning of measurement and its concentration does not change during the irradiation. Its origin is not clear. A second adduct, with EPR parameters, $a_N = 1.34\,\text{mT}$ and $g = 2.0062$, increased its concentration continuously during the irradiation and its EPR parameters correspond very well to a carbon-centred radical with an hydroxyl group (=COH) and less with a carboxyl group (–RCO). This implies the possibility that the carbon-centred radical (probably $^{\bullet}$COH= and its corresponding counterpart from the donor) are the radical species initiating the polymerization reaction. Calculated formal kinetic parameters are given in Table I.

3.2. EPR investigations of a cross-linking photo-initiator system in the presence of a dimethacrylate monomer system

Further experiments were carried out with the dental resins commonly used in dentistry consisting of CPQ, DMAEM and a different weight rations as *bis*-GMA, UDMA, DDMA and TEGDMA. The EPR spectra observed during a 10 min irradiation are shown in Fig. 5. Two types of radical are evident. The first one

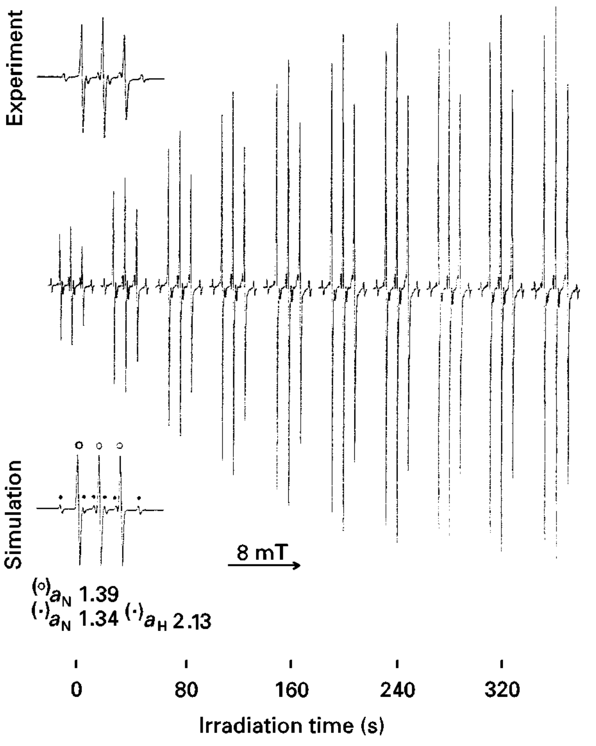

Figure 4 Kinetics of EPR spectra observed by irradiation of CPQ/DMAEM photo-initiator system (splitting constants in mT) in the presence of nitrosodurene spin trap. Upper inset: experimental spectrum; lower inset: simulated spectrum.

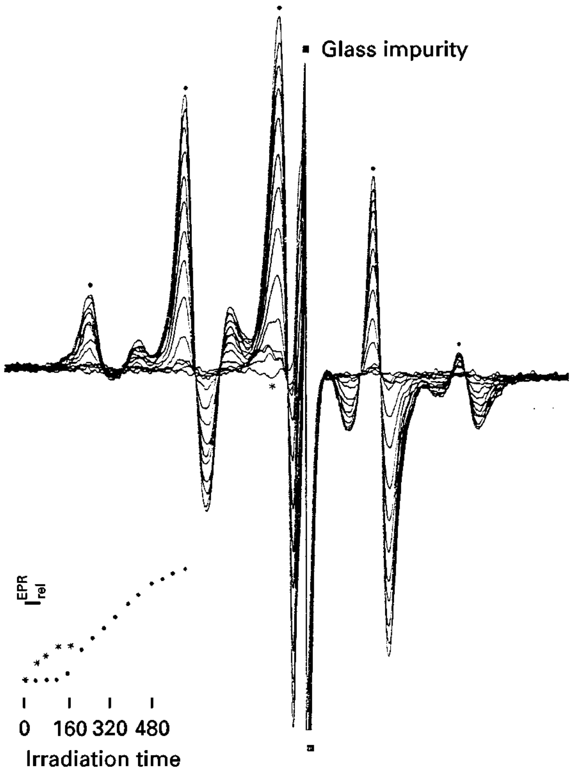

Figure 5 Kinetics of EPR spectra observed by irradiation of CPQ/DMAEM photo-initiator system in mixture of commonly used dental resins (*bis*-GMA, UDMA, DDMA and TEGDMA). The inset shows the kinetics of radicals originated from the initiator (∗) and radicals originated from the dental resins (●).

originated from the initiator. It is dominating in the first stage of irradiation in the magnetic field region ($*$). Then, with an inhibition period, a second radical or radical mixture (●) is dominating, which, according to the data in the literature, is characteristic of growing methacrylate radicals [13]. Their approximately stationary concentration was established after 15 min and their decay was followed for several hours in both samples (Samples 1 and 2; for formal kinetic parameters, see Table II). Additionally, the spectrum shown in Fig. 5 contains an intense line originating from quartz glass used to prepare the EPR tubes.

4. Conclusion

In order to establish relationships between the network morphology and important physico-chemical properties in real dental materials, a simplified model resin system based on photo-cured mixtures of various dimethacrylate co-monomers have been used in this initial study. Assuming a controlling role of the cure kinetics on the morphogenesis of the networks, EPR investigation of the radical production, lifetime and decay mechanisms has been performed. The observed rate constants for radical production were in the range of $4–5 \times 10^{-5}$ mol s^{-1}. Experimental data on the lifetime of radicals existing in cured networks after removing the light source, supported the previously suggested heterogeneous character of the cure reaction in dimethacrylate copolymers, i.e. a microgelation step followed by interconnection of the microgels, with the decay half-times of several hours. The heterogeneity of the cure reaction is increased with increasing concentration of bulky, rigid *bis*-GMA monomer in the reacting mixture. Preliminary results also suggested that there is a definite acceleration of radical decay when using TEGDMA co-monomer instead of dodecanedioldimethacrylate, the interpretation of which has not been offered in this paper. The presence of unreacted C=C bonds in the cured resin is, thus, an inevitable result of network morphogenesis. It has been suggested that with its increasing concentration, *bis*-GMA is more probably incorporated in the network by only one reactive C=C site forming large bulky pendant groups, thus reducing the number of mechanically effective chains and resulting in a T_g almost independent of the *bis*-GMA concentration [14].

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References

1. K. DUŠEK, *Coll. Czech Chem. Commun.* **58** (1993) 2245.
2. I. E. RUYTER, in "Proceedings of the International Symposium on Posterior Composite Resin Dental Materials", edited by G. Vanherle and D. C. Smith (Peter Szulc, Utrecht, 1985) p. 109.
3. Y. SAIMI, K. ISHIHARA and N. NAKABAYASHI, *Polym. J.* **24** (1992) 357.
4. P. BURTSCHER, *Dent. Mater.* **9** (1993) 218.
5. G. P. SIMON, P. E. M. ALLEN, D. J. BENNETT, D. R. G. WILLIAMS and E. H. WILLIAMS, *Macromolecules* **22** (1989) 3555.
6. A. PEUTZFELDT, *J. Dent. Res.* **73** (1994) 511.
7. P. W. ATKINS, in "Physical Chemistry", 5th Edn (Oxford University Press, Oxford, Melbourne, Tokyo, 1994) p. 916.
8. M. KUČERA, in "Mechanisms and Kinetics of Radical Polymerizations" (Academia, Prague, 1992) p. 190.
9. S. LOSHAEK and T. C. FOX, *J. Am. Chem. Soc.* **75** (1953) 3544.
10. G. F. COWPERTHWAITE, J. J. FOY and M. A. MALLOY, in "Polymer Science and Technology", edited by C. C. Gebelein and P. P. Koblitz (Plenum Press, New York, 1981) p. 379.
11. J. M. ANTONUCCI and E. E. TOTH, *J. Dent. Res.* **60** (issue A) (1981) abstr. 234, 369.
12. J. L. FERRACANE and F. H. GREENER, *ibid.* **63** (1984) 1093.
13. B. RÅNBY and J. F. RABEK, in "ESR Spectroscopy in Polymer Research" (Springer, Berlin, Heidelberg, New York, 1977) p. 112.
14. J. JANČÁŘ, *J. Dent. Mater.* (1997) accepted.

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