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The effect of electron beam irradiation on PCL and PDXO-X monitored by luminescence and electron spin resonance measurements

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Abstract

The effect of electron beam irradiation in air or argon was studied on two hydrolysable aliphatic polyesters, poly(ϵ-caprolactone) (PCL) and chemically cross-linked poly(1,5-dioxepan-2-one) (PDXO-X). A secondary alkylether radical and a tertiary alkyl radical were identified by ESR in PCL and PDXO-X after irradiation in both air and argon. For the samples irradiated in air, peroxy radicals were detected in PCL but not in PDXO-X.

For irradiated PCL, the intensities in the luminescence measurements seemed to be dose-dependent. Large amounts of oxidation products were found present in the PDXO-X irradiated in air and the luminescence intensities seemed to be dose-dependent. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Electron beam irradiation; Luminescence; Electron spin resonance

1. Introduction

Biodegradable polymers are an important group of biomedical materials continually finding new applications. The class of polymers most frequently used in this field is probably the aliphatic polyesters, due mainly to their potential to provide controlled degradability in the time range of greatest interest for important medical applications, i.e. weeks to months [1–3]. Radiation grafting of hydrophilic monomers onto many types of polymers is of general interest and has been studied in relation to biomaterial developments [4–6]. However, as a result of the radiation, the polymers are to varying extents subject to degradation and cross-linking reactions [7]. Parameters such as morphology, chemical structure of the polymer, dose and irradiation media determine whether cross-linking or chain-scission is the dominating effect of the irradiation.

In this work, two hydrolysable aliphatic polyesters, poly(ϵ-caprolactone), PCL, and chemically cross-linked poly(1,5-dioxepan-2-one), PDXO-X, were subjected to electron beam, EB, irradiation in air or argon. The chemical structures of PCL and PDXO-X are outlined in Scheme 1. Both are biodegradable polymers; PCL is well established in the market but PDXO-X is an experimental resin developed at our laboratory.

PCL and PDXO-X resemble each other in their chemical architecture but PCL is semicrystalline and PDXO-X is fully amorphous. Another difference between the two polymers is that PDXO-X is chemically cross-linked in order to achieve good form stability and good mechanical properties upon partial hydrolysis of the ester bonds.

The intention of this work was to determine the effect of EB irradiation on cross-linking and chain-scission. The aim was also to identify the species formed during irradiation using luminescence and electron spin resonance (ESR) measurement techniques.

2. Experimental

Poly(ϵ-caprolactone) (PCL): PCL in the form of granules was of commercial grade, (TONE® 787) and was kindly supplied by Union Carbide. $\overline{M}_n = 130\,000\ \mathrm{g\,mol^{-1}}$ as measured by SEC, using polystyrene calibration, and the crystallinity was 52% by weight as measured by DSC. The granules were blow moulded to a film thickness of $30 \pm 2\ \mu\mathrm{m}$.

1,5-Dioxepan-2-one (DXO): Tetrahydro-4H-pyran-4-one (THP) was made through Friedel–Craft acylation of ethylene with chloroproponyl chloride followed by ring closure

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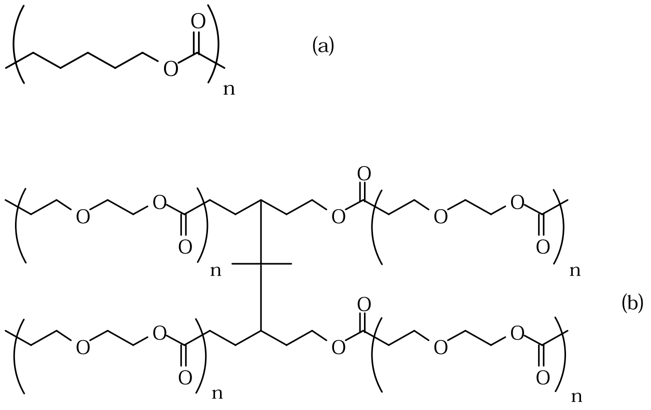
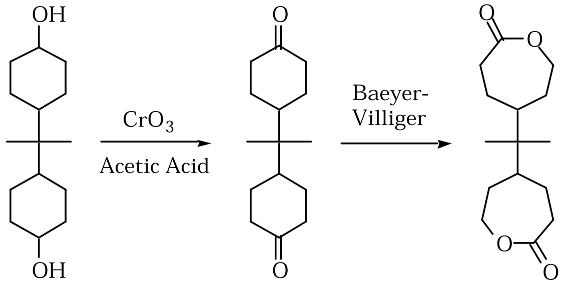


Scheme 1. The chemical structures of (a) PCL and (b) PDXO-X.

[8]. THP, 55 g (0.55 mol) was added to a slurry of 160 g of 70% *m*-chloroperbenzoic acid (0.75 mol) and 82 g (1 mol) sodium bicarbonate in 800 ml dry methylene chloride. The slurry was kept under constant stirring at 0°C while THP was added and was then maintained at 20°C for 16 h. After filtration, the methylene chloride phase was washed with sodium bisulphite and sodium bicarbonate to eliminate any remaining peracid. The methylene chloride phase was evaporated to give a slightly yellow oil. Distillation under reduced pressure (68°C, 1 mbar) gave an 80% yield of DXO. Before polymerization, DXO was recrystallized twice in anhydrous diethylether.

2,2-Bis(ϵ-caprolacton-4-yl)-propane (BCP): An isomeric mixture of 2-bis(4-hydroxycyclohexyl)-propane (54.0 g) was dissolved in 250 ml of glacial acetic acid. To this solution, under stirring and cooling at 17–18°C, there were added, drop by drop over a period of about 2 h, 55.0 g CrO_3 in an aqueous acetic acid (250 ml of glacial acetic acid and 40 ml of water). After reaction for another hour, 250 ml of 2-propanol was added under water cooling, and the solution was then allowed to stand overnight. Concentration under reduced pressure and pouring the remaining product into water precipitated powdery white crystals. After filtration and drying, 41.0 g (78%) of the crude diketone was obtained, m.p. 160–163°C. Recrystallization from benzene raised the melting point to 163°C. Bayer–Villiger oxidation was then performed by adding *m*-chloroperoxybenzoic acid (55.8 g, 0.259 mol) in batches to a stirred solution of dicyclohexyl-4,4′-dion in methylene chloride. The BCP was purified through recrystallization in 2-heptanone at an overall yield of 70%. The overall synthesis of BCP is outlined in Scheme 2.



Scheme 2. The overall synthesis route for BCP.

PDXO-film cross-linking: Cross-linking was achieved through polymerization in the melt of DXO with a cross-linking agent (16 mol%) and initiator in a steel form at 180°C for 5 min, yielding a film thickness of 0.5 mm. The cross-linking agent was BCP and ethyl (2-hexylhexanoate) was used as initiator for the transesterfication. DXO, BCP and initiator were dissolved in methylene chloride and the solvent was evaporated to give a white powder. The powder was dried in vacuum for 24 h prior to polymerization. Data on chemical characterization for the various species synthesized (DXO, BCP) has previously been published [9].

Irradiation: EB irradiation was performed with a 6.5 MeV pulsed electron accelerator (Microtrone, Acceleratorteknik, The Royal Institute of Technology, Stockholm). The samples were irradiated to a dose between 0.5 and 20 Mrad on a cooling plate kept at 2.5°C in air or in argon atmosphere at an average dose rate of 0.83 Mrad/min. Immediately after irradiation, the samples were stored in liquid nitrogen.

Swelling- and gel-measurements of PDXO-X: Various corrections for the swelling behaviour of rubber have been suggested, e.g. by Parks and Brown [10]. They calculated the swelling value Q according to the equation

$$Q = \frac{(\text{swollen weight} - \text{dried weight})}{(\text{original weight} \times 100/\text{formula weight})} \tag{1}$$

The formula weight is the total weight of the elastomer plus the weight of compounding ingredients based on 100 parts of elastomer. A comparison between cross-linking effects may then be made based on the reciprocal of the swelling value, $1/Q$.

Swelling experiments on PDXO-X samples (thickness 0.5 mm, diameter 5 mm) were carried out at room temperature. The degree of swelling was measured by weighing the samples before and after a swelling period of two days in chloroform. Equilibrium swelling was reached after 24 h.

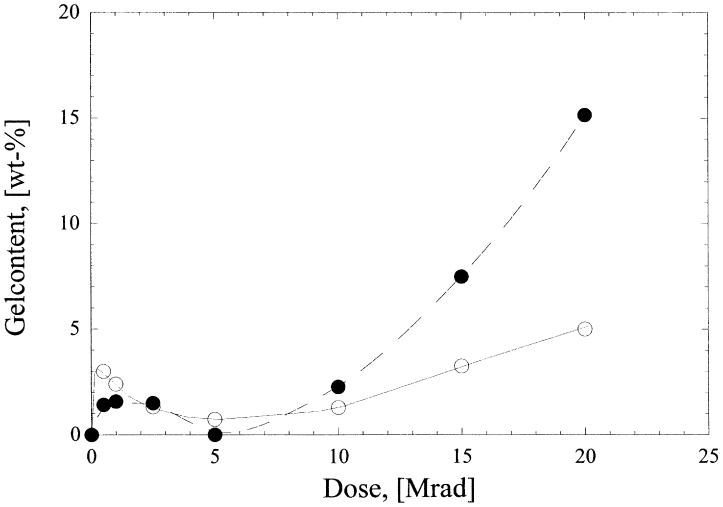


Fig. 1. The insoluble weight fractions of PCL plotted versus irradiation dose (○) irradiated in air (●).

The solute was collected and analysed by SEC. The swelling volume was calculated using the densities: chloroform 1473 kg/m^3 and PDXO-X 1100 kg/m^3. Gel percentages were determined gravimetrically after drying the swollen gels for a period of 48 h under ambient conditions followed by drying in vacuum at RTP for 48 h.

Gel-measurements on PCL: The PCL samples were placed in chloroform for 2 h at RTP. The solutions were filtrated through a 45 μ filter into pre-weighed glass-vials. The solutions were allowed to evaporate and were then dried in vacuo at RTP for 48 h. The weight of the remaining PCL in each vial was calculated and the samples were analysed by SEC.

Size exclusion chromatography (SEC): The molecular weight measurements on PCL were made at 25°C with three mixed C μ-styragel columns from Polymer Laboratories covering an MW range of 8×10^2–1.0×10^6 for poly(styrene). THF was used as solvent with a flow rate of 1.0 ml/min. A Waters instrument model 510 equipped with an automatic injector WISP 710 B was used with a differential refractometer (Waters 410) as detector. For data recording and calculations, a Copam PC-501 Turbo unit was used. The calibration was obtained from narrow MWD polystyrene standards, from which relative molecular weight averages for the samples were calculated.

Differential scanning calorimetry (DSC): DSC analysis was performed with a Perkin–Elmer DSC-7. The samples were heated to 80°C and then cooled at 20°C/min to −100°C. After 2 min equilibration, the heating scan was recorded at 10°C/min to 80°C [11].

Luminescence measurements: The measurements were made with a CLD100 chemiluminescence detector from Tohuko. Prior to the measurements, the sample chamber was purged with nitrogen at room temperature. The emitted luminescence was recorded as the temperature was increased from RT to 150°C at a rate of 20°C/min. Details concerning the instrument have been described elsewhere [12].

Electron spin resonance (ESR) measurements: The irradiated polymer films were transferred from the liquid nitrogen storage to a Teflon rod holder, 4.5 mm in diameter, and subsequently immersed in liquid nitrogen in a ESR quartz dewar flask in less than 1 min. ESR measurements were performed on a Bruker ER200D-SRC spectrometer operating at X-band. The microwave power was varied in the 0.006–200 mW range. Measurements were performed with a Bruker ER 4105DR double rectangular cavity.

3. Results and discussion

3.1. Gel-content and SEC analysis of PCL

PCL samples irradiated up to 20 Mrad in air or argon were analysed by SEC. The insoluble weight fractions are presented in Fig. 1 versus dose. These fractions or gel-contents are measures of the degree of cross-linking. For PCL irradiated in air at a dose of 0.5 Mrad, the gel-content was 3 wt.%. At higher doses, i.e. up to 10 Mrad, the gel-content was about 0 wt.% suggesting lesser cross-linking than at 0.5 Mrad. At doses between 10 and 20 Mrad, the gel-content of PCL irradiated in air increased from 0 to 5 wt.%, which implies a higher degree of cross-linking than at lower doses. For PCL irradiated in argon, the gel-content was 1 wt.% for a dose of 2.5 Mrad and decreased to about zero between 2.5 and 5 Mrad. At higher doses, between 5 and 20 Mrad, the gel-content increased from 0 to 15 wt.%, suggesting a higher degree of cross-linking than in the PCL irradiated in air. In a previous investigation, the gel-content of EB-irradiated linear low-density poly(ethylene) (LLDPE) was measured [13]. With increasing dose between 2.5 and 20 Mrad, the gel-content increased linearly from 0 to 8 wt.% for LLDPE irradiated in air and from 0 to 60 wt.% for LLDPE irradiated in argon. Thus LLDPE

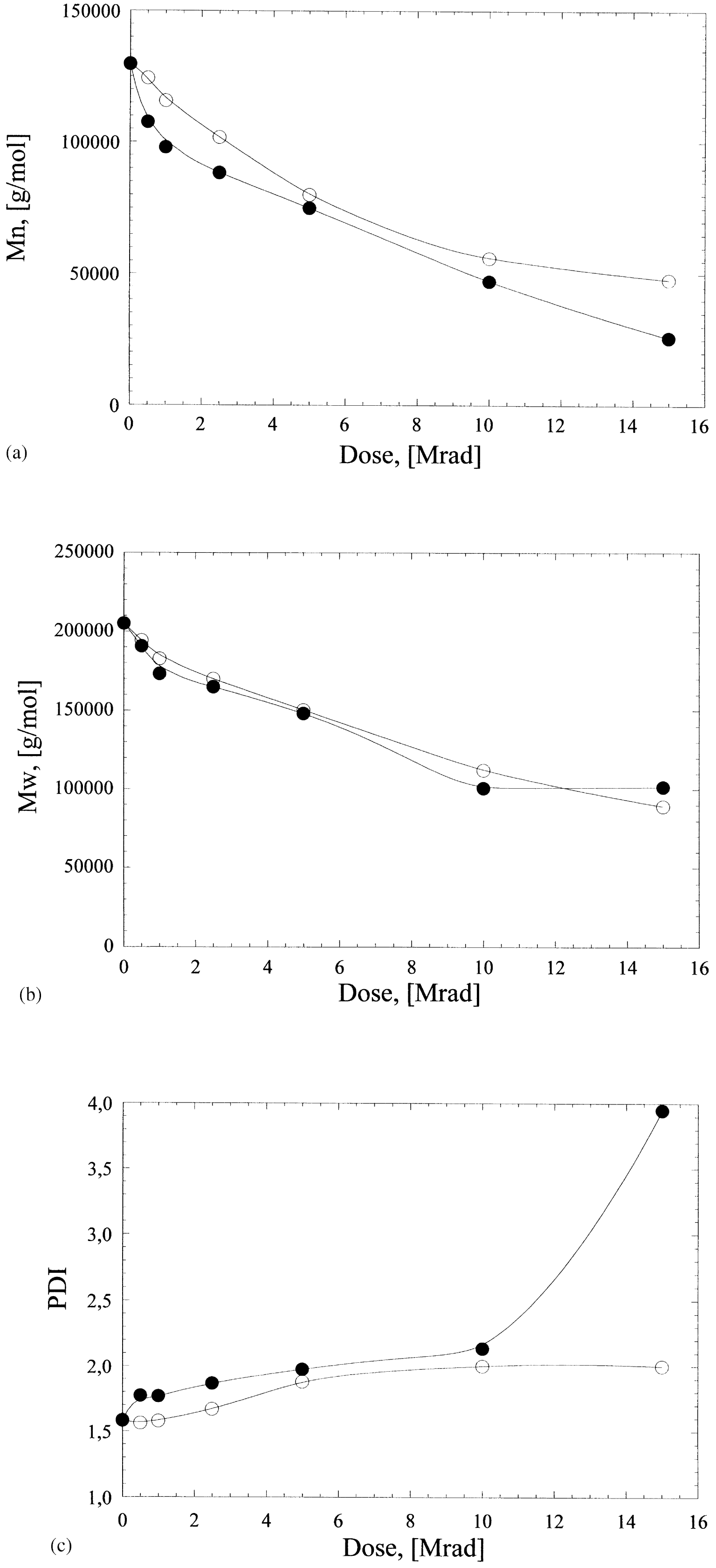


Fig. 2. (a) Number average molecular weight for the soluble fraction of PCL versus dose irradiated in air (○) and irradiated in argon (●). (b) Weight average molecular weight for the soluble fraction of PCL versus dose irradiated in air (○) and irradiated in argon (●). (c) PDI for the soluble fraction of PCL versus dose irradiated in air (○) and irradiated in argon (●).

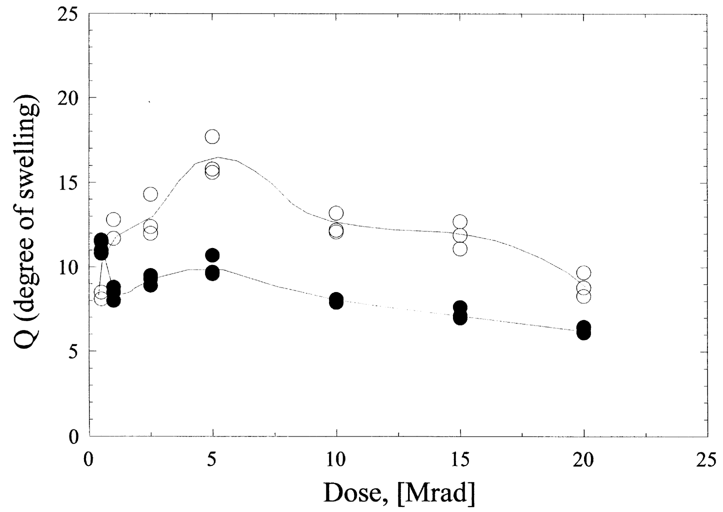


Fig. 3. Degree of swelling versus dose for PDXO-X irradiated in air (○) and irradiated in argon (●).

irradiated in both air and argon displays higher gel-contents than PCL throughout the dose range from 0 to 20 Mrad.

Average molecular weights and polydispersity indices (PDI) for the soluble fractions are displayed in Fig. 2(a)–(c) as a function of dose. None of the curves in Fig. 2(a) and (b) is reminiscent of a cross-linking system [13,14]. For irradiation of PCL in argon, the $\overline{M}_w$ curve in Fig. 2(b) and particularly the PDI curve in Fig. 2(c) indicate that gelling begins at about 15 Mrad. However, the more or less continuous decrease in $\overline{M}_n$ and $\overline{M}_w$ in Fig. 2(a) and (b), and the fact that 85 wt.% or more of the samples are soluble throughout the dose range, suggest that chain-scission is the dominating effect of the irradiation. The PDI for the PCL irradiated in air in Fig. 2(c) approaches 2.0 at higher doses, indicating random chain-scission. For the PCL irradiated in argon the PDI approaches 2.0 at a dose of 10 Mrad and then increases to about 4.0 for a dose of 15 Mrad. According to the work of Guaita et al., PDI values higher than 2.0 indicate that chain-scission at the centre of the longest molecules are disfavoured [15]. However, in the present case where cross-linking may occur, a significant increase in PDI would rather be related to the onset of gelation. This is in agreement with the increase in gel-content, particularly for PCL irradiated in argon, as shown in Fig. 1.

3.2. Swelling and gel-content analysis of PDXO-X

Since PDXO-X is a covalently cross-linked non-crystalline polymer, its properties are those of an amorphous network. In Figs. 3 and 4, the swelling and gel-content of PDXO-X irradiated in air and argon are displayed as functions of dose. In Fig. 3, it is evident that for PDXO-X irradiated in air the average swelling curve increases from 8 to 16% at a dose of from 0.5 to 5 Mrad, which corresponds to a decrease in cross-linking. At the same time, the gel-content decreases from 90 to 75%, see Fig. 4. It is therefore

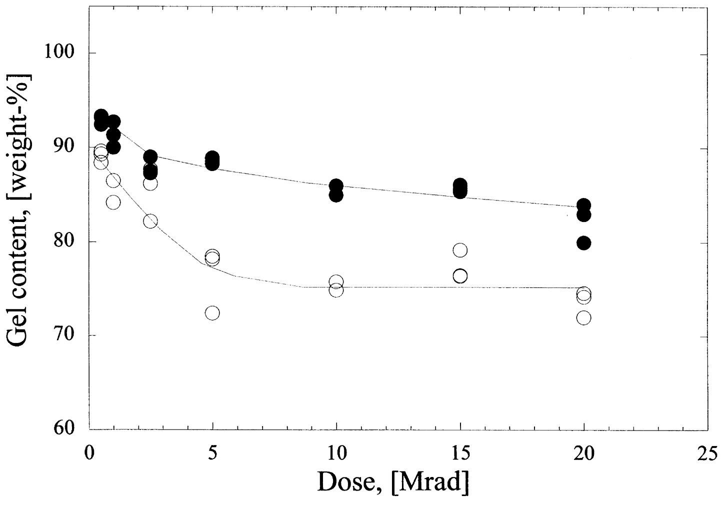


Fig. 4. Gel-content versus dose for PDXO-X irradiated in air (○) and irradiated in argon (●).

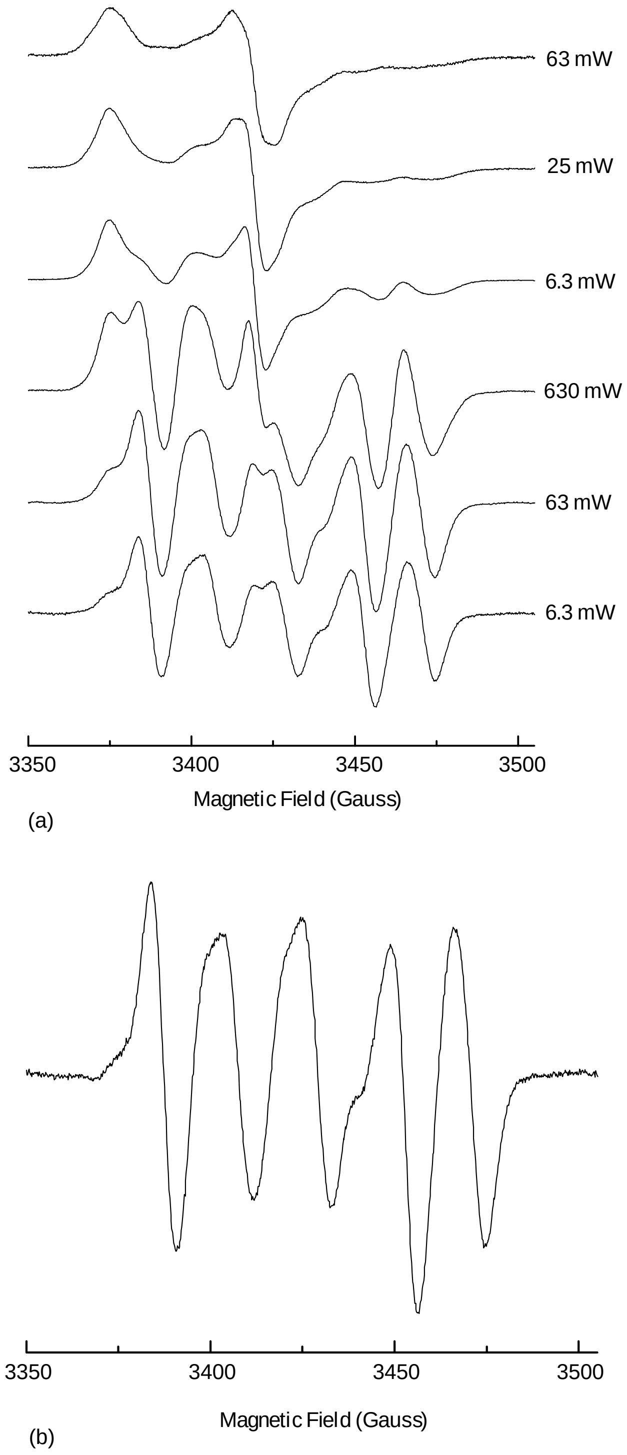
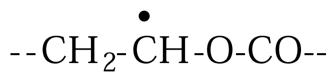


Fig. 5. (a) Microwave power dependence of the ESR-spectra of PCL irradiated in air at a dose of 15 Mrad. (b) The ESR-spectrum of PCL, irradiated in argon at a dose of 15 Mrad, after subtraction of the peroxy radical signal at 63 mW power, with an appropriate weight. The spectrum is attributed to the proposed secondary alkylether radicals.

suggested that the major effect of the irradiation, between 0.5 and 5 Mrad, is chain-scission. At a dose above 5 Mrad, the swelling in Fig. 3 and the gel-content in Fig. 4 level off, indicating a regain of cross-linking rather than chain-scission.



$$\text{--}CH_2\text{-}\dot{C}H\text{-}O\text{-}CO\text{--}$$

Scheme 3. The proposed chemical structure for the secondary alkylether radicals created in PCL as a result of irradiation.

The samples irradiated in argon are more cross-linked throughout the dose range except at a dose of 0.5 Mrad. Also in this case, there is a local swelling maximum at 5 Mrad in Fig. 3, although it is not so pronounced as in irradiation in air.

3.3. ESR-analysis

In Fig. 5(a) and (b), the ESR spectra at −196°C for PCL irradiated in air and argon are displayed. The spectra are similar to those observed for the irradiation of other aliphatic esters by Nozawa [16] and the PCL sample irradiated in air contained contributions from at least two radicals. In the ESR analysis, the different species can be separated by varying the microwave power due to their different spin–lattice relaxation times. At a low microwave power, typically 6 μW, a five-line pattern with hyperfine splitting of ca. 21 G is prominent, see Fig. 5(a). This signal is probably assignable to the structure presented in Scheme 3.

The *g*-value was found to be 2.0035, which is typical for a carbon-centred organic radical [17]. These radicals typically display *g*-values in the same range as the free electron value, 2.0023. Nozawa found upon irradiation of aliphatic esters a six-line spectrum at −196°C with hyperfine splitting of ca. 33 G [16]. This ESR-signal decayed rapidly with increasing temperature showing that it originated from a relatively unstable radical. At ambient temperature, the spectrum converted into a five-line spectrum, very similar to that observed by us for PCL at −196°C, see Fig. 5(b). According to Nozawa, the hyperfine splitting was 22–25 G depending on the number of CH_2 groups in the monomer subunit [16]. In this study, we observed no six-line spectrum, probably because the sample was exposed to RTP for about 1 min during mounting of the sample in the ESR-cell, which allowed the most unstable radicals to decay. However, in this investigation the aim was primarily to find radicals with longer times of survival under ambient conditions.

At 6.3 μW, in Fig. 5(a), the spectrum from the proposed secondary alkylether radicals, shown in Scheme 3, is prominent but a contribution from peroxy radicals is also visible. At 63 mW, the signal due to the peroxy radicals completely dominates and other signals are broadened.

A peroxy radical was identified in PCL irradiated in air. At high microwave power in Fig. 5(a), typically 60 mW, the line shape of the five-line spectrum is saturated and a line shape typical of peroxy radicals is observed. The *g*-values were determined to be $g_1 = 2.035$, $g_2 = 2.009$ and $g_3 = 2.005$. These can be compared with previously observed *g*-values for peroxy radicals in other types of polymers, $g_1 = 2.035–2.045$, $g_2 = 2.007–2.024$ and $g_3 = 2.002–2.007$ [17].

The ESR spectra at −196°C of PDXO-X irradiated in air and argon are displayed in Fig. 6. Only carbon-centred radicals were observed even after EB irradiation in air. The *g*-value was measured to 2.0032 and no separation of different spectral contributions could be detected with varying microwave power.

The spectra in Fig. 6 remained unchanged in the power range 6.3–200 mW, apart from the normal line broadening with increasing microwave power. The signal is attributed to the proposed tertiary alkyl radicals in Scheme 4. Exposure of the PDXO-X-film to air at 20°C for several hours had no effect on the line shape and only a small decrease in signal intensity was observed. Further warming to 80°C for 5 min resulted in a decrease in the signal intensity by 70%, but it had no effect on the spectral line shape. The high temperature stability in air suggests a relatively stable radical, indicating a sterically hindered position and a low chain mobility of the densely cross-linked PDXO-X matrix. Moreover, the separation between the resolved spectral lines is small, 12–13 G, which implies a tertiary carbon-radical [18]. The only tertiary carbon in PDXO-X is in the cross-link sites and it is therefore suggested that the spectra in Fig. 6 originate from the radical structure presented in Scheme 4.

3.4. Luminescence-measurements

In the interpretation of the measurements, it is necessary to consider that the luminescence intensity reflects multiple reactions in the sample, as the temperature is increased in the luminescence analysis. For EB-irradiated polymers, the emitted light consists of thermoluminescence (TL) from recombination of charges and radicals as well as chemiluminescence (CL) from chemical reactions of hydroperoxides and peroxy radicals [19–21]. The interference of TL in CL-measurements has been pointed out by Mendenhall [22]. Electron beam irradiation yields different kinds of charged species and it is not possible from luminescence measurements alone to discriminate between the reaction of two radicals or of two oppositely charged atoms.

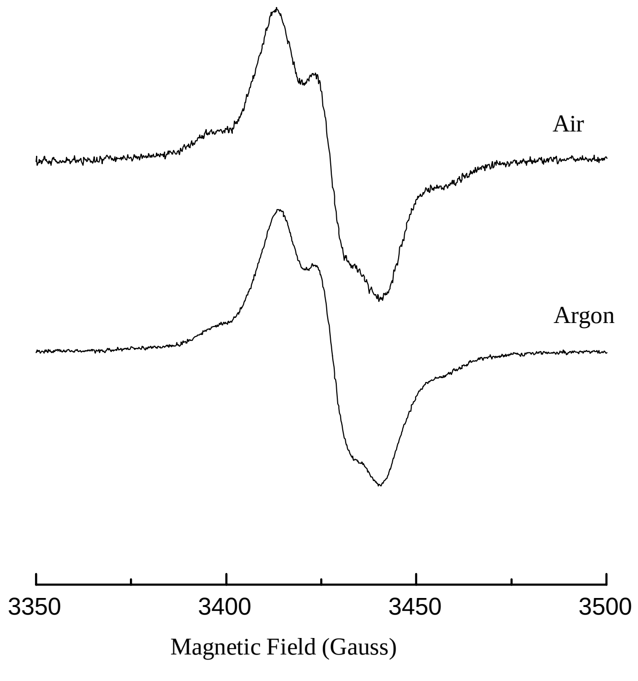
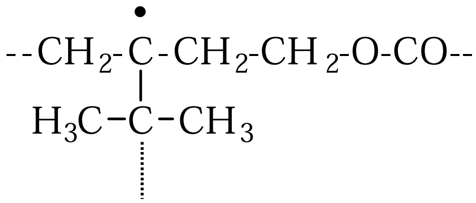


Fig. 6. ESR-spectra of PDXO-X irradiated at a dose of 15 Mrad in air and argon.



$$-\!-CH_2-\overset{\bullet}{C}-CH_2-CH_2-O-CO-\!- \\ H_3C-C-CH_3$$

Scheme 4. The proposed chemical structure for the tertiary alkyl radicals created in PDXO-X as a result of irradiation.

In Fig. 7(a) and (b), the luminescence intensity and temperature for PCL irradiated in air and argon with different irradiation doses are plotted versus time. The intensity seems to be approximately proportional to the dose. A sharp peak can be observed after 180–200 s when the temperature has reached 60–70°C. The intensity drops dramatically just above this temperature range, and a second peak or shoulder emerges after about 250 s corresponding to a temperature of about 90°C. It is not possible to differentiate between the shapes of the luminescence curves for PCL irradiated in air and in argon in Fig. 7(a) and (b). From the ESR measurements on PCL irradiated in air it was concluded that two types of radicals were present, viz. alkylether radicals (see Scheme 3) and peroxy radicals. Since the melting point for PCL is about 60°C, it is suggested that the second peak in Fig. 7(a) and (b) represents a higher recombination ratio of the radicals as the material melts, i.e. the melting has a burst effect on the remaining radicals.

PDXO-X irradiated in air displays two luminescence signals, see Fig. 8(a); one just after 200 s at a temperature of about 80°C and another after 600 s at a temperature of 150°C. From the ESR-measurements on PDXO-X irradiated in air and argon, only one type of radical could be detected, see Scheme 4, and the interpretation is therefore that the first signal in Fig. 8(a) corresponds to the recombination of the tertiary carbon-centred radical. The luminescence intensity for the signals at 200 s in Fig. 8(a) does not change significantly with dose. This suggests that PDXO-X is saturated with the type of radical displayed in Scheme 4 at a dose of 2.5 Mrad or lower, i.e. higher doses do not yield significantly more radicals of this type, or only a certain amount of this radical is stable in the PDXO-X matrix independent of dose. Moreover, the same luminescence intensity at different doses for the signals at

200 s in Fig. 8(a) indicates that the different degrees of cross-linking as a result of the dose according to Figs. 3 and 4 will not affect the recombination of these radicals at 80°C. Other types of radicals that might form, i.e. primary and secondary alkoxy radicals, will probably recombine prior to detection with CL.

In case of PDXO-X irradiated in argon in Fig. 8(b) the signal at 200 s seems to be dose dependent. Furthermore the luminescence curve in Fig. 8(b), does not give a signal at 600 s, which suggests that the signal in Fig. 8(a), at this time, corresponds to the cleavage and recombination of oxidation products culminating at a temperature of 155°C. It is interesting to note that these oxidation products do not correspond to peroxy radicals, i.e. no peroxy radicals were detected in the ESR measurements. Furthermore, in Fig. 8(a) the signal at 600 s yields greater intensities as the dose increases, indicating that the amount and rate of decay for the oxidation products increase with increasing dose.

4. Conclusions

A secondary alkylether radical and a tertiary alkyl radical were detected in PCL and PDXO-X, respectively, irradiated in argon as measured by ESR. In the case of the corresponding samples irradiated in air, peroxy radicals were detected in PCL but not in PDXO-X. The luminescence measurements revealed a dose-dependence for the luminescence intensities of the radicals in PCL, irradiated in air and

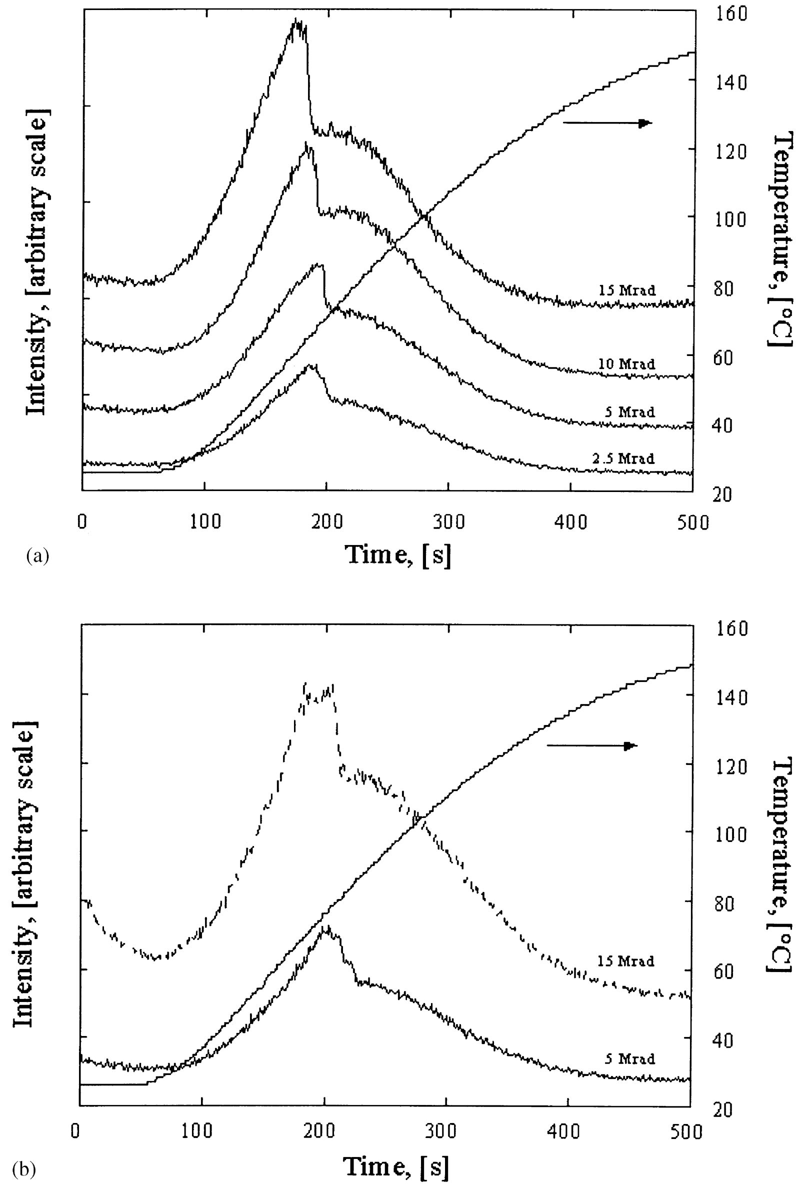
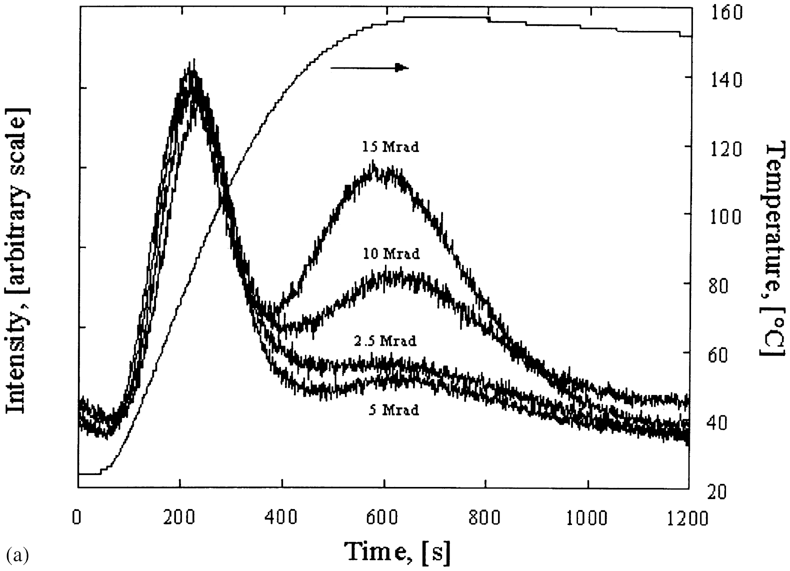
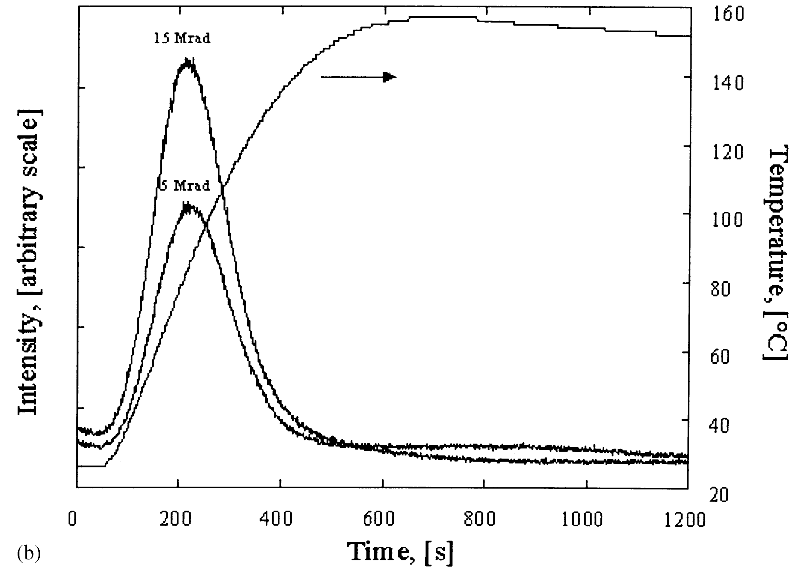


Fig. 7. (a) The luminescence intensity and temperature for PCL irradiated in air plotted versus time for different doses; 2.5, 5, 10, and 15 Mrad. (b) The luminescence intensity and temperature for PCL irradiated in argon plotted versus time for different doses; 5 and 15 Mrad.



(a)



(b)

Fig. 8. (a) The luminescence intensity and temperature for PDXO-X irradiated in air plotted versus time for different doses; 2.5, 5, 10, and 15 Mrad. (b) The luminescence intensity and temperature for PDXO-X irradiated in argon plotted versus time for different doses; 5 and 15 Mrad.

argon. It was not possible to differentiate between the secondary alkylether radicals and the peroxy radicals in PCL irradiated in air as measured by CL. Large amounts of oxidation products were found to be present in PDXO-X irradiated in air in spite of the absence of peroxy radicals in the ESR analysis. The intensities of the oxidation products seemed to be dose-dependent.

Acknowledgements

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