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Studies on the effect of electron beam radiation on the molecular structure of ultra-high molecular weight polyethylene under the influence of α-tocopherol with respect to its application in medical implants

M. PARTH, N. AUST*, K. LEDERER
Department of Chemistry of Polymeric Materials, University of Leoben,
Franz-Josef-Str 18, A-8700 Leoben, Austria
E-mail: aust@unileoben.ac.at

Ultra-high molecular weight polyethylene (UHMW-PE) is being used successfully for articulating surfaces in joint endoprostheses, especially for cups of total hip endoprostheses. Sintered specimens containing various amounts of α-tocopherol (vitamin E) as a biocompatible stabilizer, were irradiated in nitrogen atmosphere as well as in air with various dosages of electron beam radiation.

Size exclusion chromatography (SEC) was used to analyze the soluble fractions of the UHMW-PE samples according to their molecular weight distribution prior to and after irradiation.

In nitrogen atmosphere the radiation-induced crosslinking showed to be dependent on the added amount of α-tocopherol in the sintered specimens. With an increasing content of α-tocopherol, the stabilizer acted as a scavenger for free radicals. Thus, the crosslinking was more and more hindered. The same effect was observed on the samples irradiated in air, where, in addition to the crosslinking process, oxidative molecular degradation occurred. The highest extent of crosslinked material was yielded with unstabilized samples in nitrogen atmosphere.

1. Introduction

Since the 1960s, ultra-high molecular weight polyethylene (UHMW-PE) has been used as a material in medical implants, especially for cups in hip endoprostheses [1]. Since then, attempts to characterize and to improve the polymeric material have been carried out since UHMW-PE may undergo *in vivo* oxidation [2–5] leading to molecular degradation [6] accompanied by an increase in brittleness of the material.

The degraded UHMW-PE leads to high wear and debris in the surrounding of the affected implant [7]. This may cause inflammation of the tissue, followed by osteolysis [8].

To avoid these effects, attempts have been made since the 1980s to form an ''ideal'' material for medical implants. A promising method to reach this goal is to provoke the crosslinking of the material with high-energy radiation, e.g. electron beam radiation [9].

The effects of high-energy radiation on polyethylene have been studied extensively since the late 1950s by Charlesby [10] and Chapiro [11]. Under the influence of γ-radiation in an inert atmosphere or vacuum, which is commonly used for the sterilization of endoprostheses made of UHMW-PE, the predominant effect is crosslinking, whereas in the presence of air, oxidative molecular degradation becomes more important. In the case of irradiation with electron beams, the oxidative degradation becomes negligible except on the surface of the material [12]. The reaction mechanism leading to either oxidative molecular degradation or crosslinking of polyethylene were summarized by Singh in 1999 [13].

The effects of high-energy radiation on the mechanic and spectroscopic properties of irradiated UHMW-PE have been investigated extensively [14, 15], as well as the properties of the insoluble gel network, e.g. the crosslinking density [16].

Since only few publications deal with the molecular characteristics of the irradiated material [6, 17], the intention of this work was to study the effect of electron beam radiation on the degree of crosslinking and its influence on the molecular weight distribution of the not crosslinked soluble fraction of the UHMW-PE.

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*Author to whom all correspondence should be addressed.

Furthermore, the influence of α-tocopherol as a biocompatible stabilizer in UHMW-PE [18–20] on the changes in the molecular weight distribution and the degree of crosslinking was investigated in air and in inert nitrogen atmosphere.

2. Materials and methods

2.1. Sample preparation

The UHMW-PE powder ''Hostalen GUR 1020'' (LOT No.: B15331047) was a product of Hoechst AG, Frankfurt/Main, Germany, now commercially available from Ticona GmbH, Frankfurt/Main, Germany, under the tradename ''GUR 1020''. The α-tocopherol (LOT No.: 606876) was delivered from Hoffmann-LaRoche AG, Basel, Switzerland. The UHMW-PE powder was homogeneously mixed with α-tocopherol as a biocompatible stabilizer (mass content: 0%, 0.2%, 0.4%, and 0.8% (w/w)) and was sintered for 7 h at a temperature of 220 °C and a pressure of 35 bar at Isosport GmbH, Eisenstadt, Austria, producing plates with a thickness of 60 mm and a diameter of 600 mm.

The samples for the determination of the solubility and the molecular weight distribution were taken from microtome sections about 500 μm below the surface of these plates.

2.2. Electron beam irradiation

For the irradiation experiments, cubical specimens with an edge length of 20 mm were cut out from the sintered plates and placed in round-bottomed flasks. In the case of the experiments carried out in nitrogen atmosphere, the flasks were flushed several times with nitrogen with subsequent evacuation by the aid of a rotary vacuum pump to ensure the absence of oxygen. The nitrogen used was purified with the Oxisorb gas-cleaning system (Linde AG, Höllriegelskreuth, Germany) and contained less than 0.0001% (v/v) of oxygen.

The electron beam radiation was carried out at Mediscan GmbH, Kremsmünster, Austria, with the 10 MeV linear accelerator TB-10/15 from Titan Beta, Dublin, CA, USA. The absorbed dosage (10–100 kGy) was determined photometrically according to an internal standard procedure of Mediscan [21].

2.3. Size exclusion chromatography (SEC)

The molecular weight distributions of the UHMW-PE samples were determined at 135 ± 0.02 °C with the ''GPC 220'' chromatograph (Polymer Laboratories, Church Stretton, UK) equipped with a differential refractive index (DRI) detector (Polymer Laboratories, Church Stretton, UK), and a differential viscometer 210 R (Viscotek, Houston, TX, USA); furthermore, the unit was coupled with a low-angle laser light scattering (LALLS) photometer KMX 6 ($\lambda = 633$ nm) (Chromatix, Sunnyvale, CA, USA). A schematic of the SEC apparatus is shown in Fig. 1. A set of two identical columns was used, packed with crosslinked styrene-divinylbenzene (PLgel Mixed-A LS, particle size: 20 μm, length: 300 mm, inner diameter: 7.5 mm; Polymer Laboratories, Church Stretton, UK).

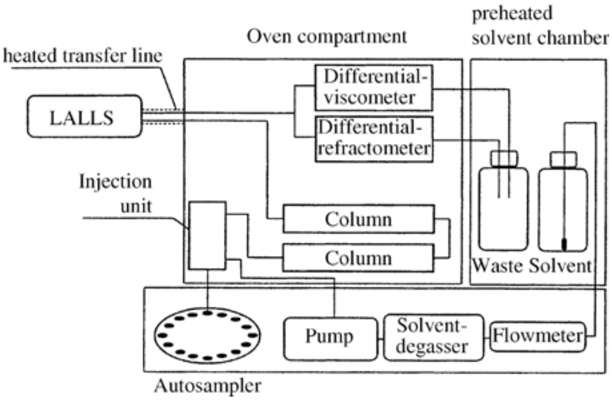

Figure 1 Schematic of the chromatograph used for the determination of the molecular weight distribution.

1,2,4-Trichloro benzene (Merck, Darmstadt, Germany) containing 0.0125% (w/v, mixed at room temperature) 2,6-di-tert.-butyl-(4-methylphenol) (BHT) was used as solvent and as eluent after filtration through a 0.45 μm poly(tetrafluoro ethylene) (PTFE) filter. Prior to entering the pump, the solvent was degassed with an online degasser PL-DG2 (Erc Inc., Kawaguchi City, Japan).

The flow rate was set to 0.2 mL/min to avoid molecular degradation [17, 22] and continuously monitored with the aid of the flow meter LiquiFlow L1-FA-11-0 (Bronkhorst, Ruurlo, Netherlands).

The polymer solutions were prepared with amounts between 1 and 2 mg of the polymer in 10 mL of the solvent and were flushed with purified nitrogen (see Section 2.2.) for 15 min at room temperature to avoid oxidative degradation during the dissolution. The samples were then placed in an oven and were rolled by a self-assembled apparatus at about 3 revolutions/min at 150 °C for 4 h prior to injection. This procedure homogenizes the samples with negligible mechanical stress. Further details concerning the determination of the molecular weight distribution are described elsewhere [17, 22].

2.4. Determination of the insoluble fraction

The gel content of the samples was determined by placing disk specimens of a diameter of 10 mm and a thickness of about 300 μm in an excess of 50 mL of 1,2,4-trichloro benzene containing 0.0125% (w/v) BHT for 3 h at 145 °C under nitrogen atmosphere. The specimens were then dried for 24 h in a vacuum oven at 80 °C and a pressure of 1 mbar. The remaining insoluble polymer content was determined gravimetrically.

The ratio of molecular degradation and crosslinking $G(S)/G(X)$ was calculated according to Charlesby and Pinner [23]:

$$s + \sqrt{s} = \frac{G(S)}{2G(X)} + \frac{100 \cdot N_{\mathrm{A}}}{M_{\mathrm{w},0} \cdot G(X) \cdot D} \qquad (1)$$

where s is the soluble fraction; $G(S)$ is the number of broken main chain bonds per 100 eV; $G(X)$ is the number of newly formed intermolecular linkages per 100 eV; $M_{\mathrm{w},0}$ is the weight average molecular weight of the initial sample; D is the absorbed dosage in eV per gram, and N_{A} is the Avogadro's constant ($= 6.023 \cdot 10^{23}$ per mole).

3. Results and discussion

Analyzing samples that were irradiated with different dosages of electron beam clearly shows a dependency of degradation and crosslinking on the absorbed dose. Fig. 2 shows the curves relating the soluble fraction s and the absorbed dosage D. According to Equation 1, Fig. 2 shows the plot of $s + s^{1/2}$ versus $1/D$ for four different cases: an unstabilized sample irradiated in nitrogen atmosphere and air, and a sample stabilized with 0.8% of α-tocopherol in nitrogen atmosphere and air.

As can be seen from Fig. 2, the soluble fraction of the polymer, represented by the term $s + s^{1/2}$, never disappears completely; it follows Equation 1 and reaches at an infinite dose, the value of $G(S)/2G(X)$, which represents the ratio of molecular degradation to crosslinking. For the unstabilized samples irradiated in nitrogen, this value turned out to be 0.18 which is in good agreement with the reported values of 0.9 for $G(S)$ and 3 for $G(X)$ [24].

The same samples irradiated in air show curves shifted towards higher values of $s + s^{1/2}$ which indicates that the ratio of $G(S)/2G(X)$ has changed. Here, the crosslinking predominates slightly less over the molecular degradation.

Quite different is the situation in the case of the stabilized samples. The slopes of these curves are approximately twice as large as for the unstabilized samples. Due to these higher slopes the value of 2 for $s + s^{1/2}$ is reached at lower values of $1/D$ compared to the unstabilized samples. This means that a higher radiation dosage in the case of the stabilized samples is necessary to reach the same amount of insoluble material as for the unstabilized samples.

Table I summarizes the values of $s + s^{1/2}$ as well as $G(S)/G(X)$ for the investigated samples. The limiting sol fraction is the lowest possible content of sol at an infinite absorbed radiation dose and can be obtained from the intercept of the $s + s^{1/2}$ axis in Fig. 2 by substitution of s by x^2 and resolving the quadratic equation. From this value of s, the limiting gel fraction in percent is calculated: $(1 - s) \cdot 100$. As can also be seen from Table I, the ratio of $G(S)/G(X)$ never exceeds the value of 0.88. As it was shown by Charlesby *et al.* [23], for all ratios of $G(S)/G(X) < 4$ crosslinking predominates over molecular degradation. Under the conditions of these experiments, there is no danger of molecular degradation of the UHMW-PE samples without simultaneous crosslinking. To obtain a product that possesses the highest extent of crosslinking, conditions with a low ratio of $G(S)/G(X)$ should be preferred.

TABLE I Values of $s + s^{1/2}$ and $G(S)/G(X)$ according to Charlesby and Pinner as well as the limiting gel fraction (see text) for the unstabilized and stabilized (content of α-tocopherol: 0.8%) sintered UHMW-PE samples irradiated in air and nitrogen atmosphere with electron beam

Sample	$s + s^{1/2}$ at $1/D = 0$	$G(S)/G(X)$	Limiting gel fraction/%
Unstabilized/nitrogen	0.17	0.34	98
Unstabilized/air	0.30	0.60	94
Stabilized/nitrogen	0.25	0.50	96
Stabilized/air	0.44	0.88	89

As can be seen from Fig. 3, the influence of the stabilizer concentration turned out to decrease with an increasing dosage and seemed to disappear completely at an absorbed dose D of 100 kGy leading to a gel fraction of almost 100%. This indicates that at this point α-tocopherol is no longer able to impede crosslinking. The dependency of the extent of gel fraction on the absorbed dose for the three samples with different stabilizer content (see Fig. 3) does not differ as much as each of them deviates from the unstabilized sample.

Due to the same reaction mechanism the effects caused by γ-irradiation [17] and electron beam of the same dosage lead to comparable results. The samples irradiated with 22 kGy of electron beam in nitrogen show a good agreement with the samples from the γ-sterilization (25 kGy, nitrogen atmosphere).

Typical molecular weight distribution curves of the native polyethylene powder and the soluble fraction of the sintered samples stabilized with 0.8% α-tocopherol prior to and after electron beam irradiation with 10, 22, and 100 kGy in nitrogen atmosphere are shown in Fig. 4.

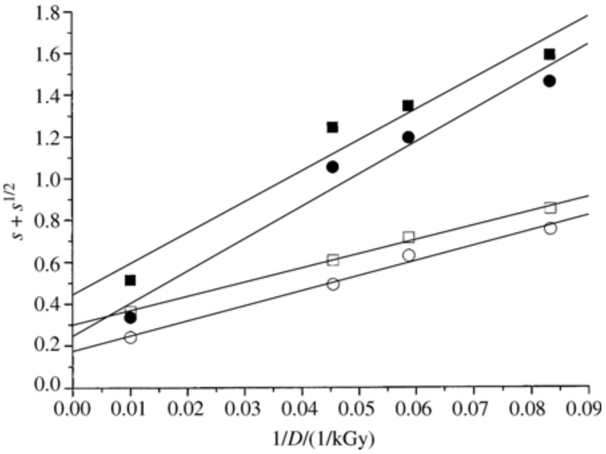

Figure 2 Plot of $s + s^{1/2}$ as a function of $1/D$ according to Charlesby and Pinner (see text and Equation 1). Stabilized (0.8% α-tocopherol; closed symbols) and unstabilized (open symbols) sintered UHMW-PE samples, irradiated in nitrogen atmosphere (○, ●) and in air (□, ■) with electron beam of varying dosage.

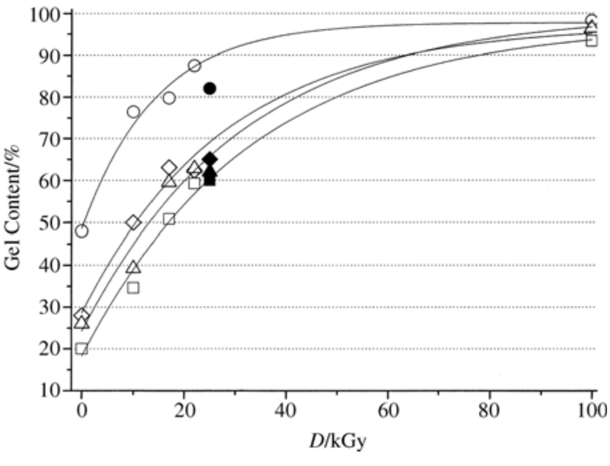

Figure 3 Gel content of the sintered UHMW-PE samples with various content of α-tocopherol as stabilizer as a function of the absorbed dosage D of electron beam in nitrogen atmosphere. Content of α-tocopherol: 0% (○), 0.2% (◇), 0.4% (△), and 0.8% (□). Closed symbols: corresponding experiments with γ-irradiation used for sterilization in nitrogen atmosphere (25 kGy) (see text).

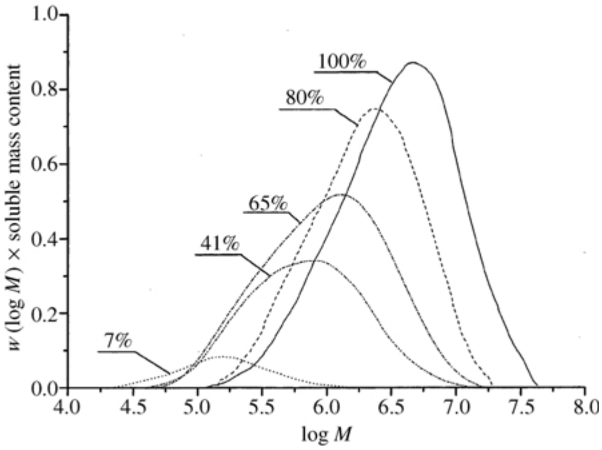

Figure 4 Molecular weight distribution curves of the native polyethylene (solid line) and the soluble fraction of the sintered UHMW-PE samples containing 0.8% α-tocopherol prior to (dashed line) and after electron beam irradiation in nitrogen atmosphere with 10 (dash dotted line), 22 (dash dot dotted line), and 100 kGy (dotted line). The areas of the distribution curves correlate to the mass content in percentage of soluble fraction of the samples.

With an increasing absorbed dosage, the molecular weight distribution is shifted towards lower molecular weight, and, caused by molecular degradation, the start of the low molecular weight tail is shifted from 45 kg/mol in case of an absorbed dosage of 10 kGy to 38 kg/mol in case of 22 kGy and finally to only 18 kg/mol with an absorbed dosage of 100 kGy.

The areas of the molar mass distribution curves in Fig. 4 correlate to the soluble mass content of the samples. The native polyethylene powder is completely soluble, sintering even without subsequent irradiation leads to an insoluble fraction of 20%. Electron beam irradiation increases the gel content up to 93% in the case of an absorbed dosage of 100 kGy.

The molecular degradation can also be observed by a decrease in the value of the weight average molecular weight, M_w. This is shown in Fig. 5 for an unstabilized and a stabilized sample containing 0.8% of α-tocopherol as a function of the absorbed dosage in nitrogen (cf. Table II). As could be seen from Fig. 2, the soluble fraction never completely disappears even at inifinite dosage. The same tendency can be observed from Fig. 5, where the weight average molecular weights reach values of about 200 kg/mol and 50 kg/mol with and without stabilizer at dosages of 100 kGy.

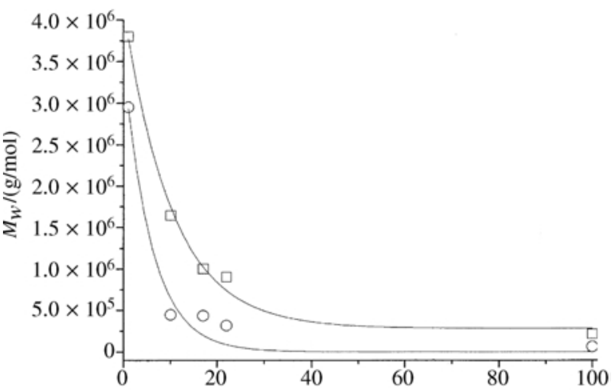

Figure 5 Weight average molecular weight of the soluble fraction of the sintered UHMW-PE samples without (○) and with 0.8% α-tocopherol as stabilizer (□) as a function of the absorbed dosage D of electron beam radiation in nitrogen atmosphere.

TABLE II Weight average molecular weight of the soluble fraction (M_w per kg/mol) of the sintered, stabilized (0.8% α-tocopherol) and unstabilized UHMW-PE samples in air and nitrogen atmosphere after irradiation with various dosages of electron beam

Dosage (kGy)	Atmosphere (stabilizer/%)			
	Nitrogen	Air	Nitrogen	Air
	0.8	0.8	0	0
10	1640	1280	445	416
17	1000	900	433	408
22	900	740	315	328
100	213	125	59	87

Comparing the samples irradiated in nitrogen to those irradiated in air it turns out that generally the soluble fraction of the samples irradiated in air is higher, which indicates that in air more molecular scission and less crosslinking occurs (cf. Table I). The ratio of $G(S)/G(X)$ in air is approximately two times higher than in nitrogen. This behavior is also reflected in lower values of the limiting gel fraction of the samples irradiated in air.

As can be seen from Table II, the weight average molecular weight of the soluble fraction of the unstabilized samples does not significantly depend on the irradiation atmosphere except in the case of 100 kGy dosage, where the soluble fraction of the sample irradiated in air shows a distinctively higher molecular weight than the one irradiated in nitrogen.

In case of the soluble fraction of the sample stabilized with 0.8% α-tocopherol it can be seen from Table II and Fig. 6 that the stabilizer loses a lot of its efficiency when the irradiation is performed in air. The samples irradiated in nitrogen show higher values for the molecular weight, however, they are less soluble as can be seen from the smaller peak area. It can be assumed that the α-tocopherol which acts as a scavenger of free radicals is used up by the oxygen molecules in the air and therefore molecular scission as well as crosslinking are less inhibited.

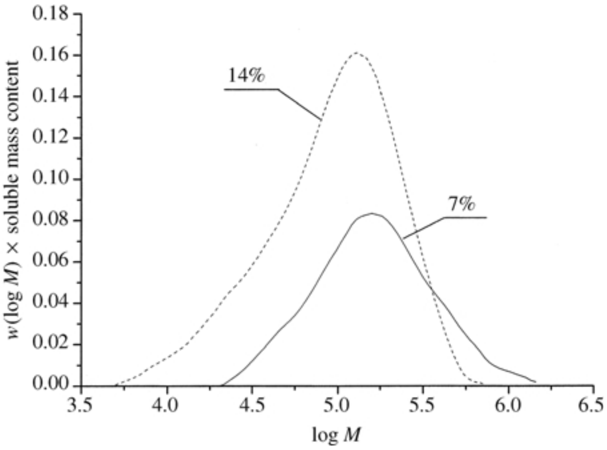

Figure 6 Molecular weight distribution curves of the soluble fraction of the sintered UHMW-PE sample stabilized with 0.8% α-tocopherol after electron beam irradiation (100 kGy) in nitrogen (solid line) and air atmosphere (dashed line). The areas of the distribution curves correlate to the mass content in percentage of soluble fraction of the samples.

4. Conclusions

UHMW-PE undergoes crosslinking and molecular degradation reactions during electron beam or γ-irradiation. The extent of crosslinking and degradation depends on the absorbed dosage of the radiation. The molar mass of the soluble fraction significantly decreases with an increasing absorbed dosage.

In nitrogen atmosphere, the crosslinking process is favored, whereas in air, molecular degradation dominates. The stabilized samples irradiated in nitrogen atmosphere show higher values of the molar mass than those irradiated in air.

α-tocopherol as a biocompatible stabilizer acts as a scavenger for free radicals. Thus, the extent of crosslinking as well as molecular degradation is reduced in both air and nitrogen atmosphere.

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References

1. W. WAUGH, in ''John Charnley – The Man and the Hip'' (Springer Verlag, Heidelberg, 1990).
2. M. GOLDMAN, R. GRONSKY, R. RANGANATHAN and L. PRUITT, *Polymer* **37** (1996) 2909.
3. E. BRACH DEL PREVER, M. CROVA, L. COSTA, A. DALLERA, G. CAMINO and P. GALLINARO, *Biomater.* **17** (1996) 873.
4. F. J. BUCHANAN, B. SIM and S. DOWNES, *Plast., Rub. and Comp. Proc. and Appl.* **27** (1998) 148.
5. L. COSTA, M. P. LUDA, L. TROSSARELLI, E. M. BRACH DEL PREVER, M. CROVA and P. GALLINARO, *Biomater.* **19** (1998) 1371.
6. P. EYERER, M. KURTH, R. ELLWANGER, H. MÄDLER, H. A. FEDEROLF and A. SIEGMANN, *Kunststoffe* **77** (1987) 617.
7. J. A. DAVIDSON and G. SCHWARTZ, *J. Biomed. Mat Res.: Appl. Biomater.* **21** (1987) 261.
8. B. ZICAT, C. A. ENGH and E. GOKCEN, *J. Bone and Joint Surg.* **77A** (1995) 432.
9. R. M. STREICHER, *beta–gamma* **1** (1989) 34.
10. A. CHARLESBY, in ''Atomic Radiation and Polymers'' (Pergamon Press, Oxford, 1960).
11. A. CHAPIRO, in ''Radiation Chemistry of Polymeric Systems'' (Interscience Publishers, New York, 1962).
12. Y. FENG and Z. T. MA, in ''Radiation Processing of Polymers'', edited by A. Singh and J. Silverman (Hanser Publishers, Munich, 1992).
13. A. SINGH, *Radiation Phys. Chem.* **56** (1999) 375.
14. Y. IKADA, K. NAKAMURA, S. OGATA, K. MAKINO, K. TAJIMA, N. ENDOH, T. HAYASHI, S. FUJITA, A. FUJISAWA, S. MASUDA and H. OONISHI, *J. Polym. Sci.* **37** (1999) 159.
15. H. M. ABOU ZEID, Z. I. ALI, T. M. ABDEL MAKSOUD and R. M. KHAFAGY, *J. Appl. Polym. Sci.* **75** (2000) 179.
16. O. K. MORATOGLU, C. R. BRAGDON, D. O. O'CONNOR, M. JASTY, W. H. HARRIS, R. GUL and F. MCGARRY, *Biomater.* **20** (1999) 1463.
17. M. PARTH, N. AUST and K. LEDERER, *Int. J. Polym. Anal. Charact.* accepted.
18. C. WOLF, T. KRIVEC, J. BLASSNIG, K. LEDERER and W. SCHNEIDER, *J. Mater. Sci.: Mater. Med.* in print.
19. C. WOLF, K. LEDERER and U. MÜLLER, ''Test of biocompatibility of α-tocopherol with respect to the use as a stabilizer in ultra-high molecular weight polyethylene for articulating surfaces in joint endoprostheses'', *ibid.* submitted.
20. S. AL-MALAIKA and S. ISSENHUTH, *Polym. Degrad. Stab.* **65** (1999) 143.
21. F. GRATZL, Mediscan GmbH, Kremsmünster, Austria, private communication.
22. N. AUST, M. PARTH and K. LEDERER, *Int J. Polym. Anal. Charact.* **6** (2001) 245.
23. A. CHARLESBY and S. H. PINNER, *Proc. R. Soc. London, Ser. A* **249** (1959) 367.
24. V. D. MCGINNISS, in ''Encyclopedia of Polymer Science and Engineering'', Vol. 4, edited by H. F. Mark, N. M. Bikales, C. G. Overberger and G. Menges (Wiley & Sons, New York, 1986), p. 432.

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