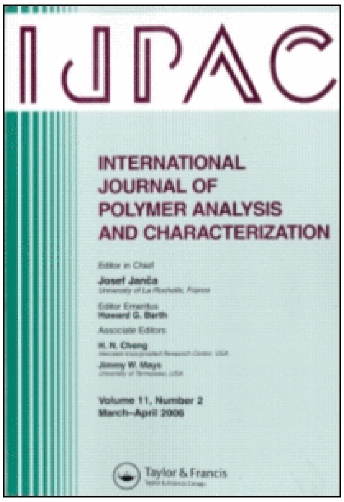

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Molecular Characterization of Ultrahigh Molar Mass and Soluble Fractions of Partially Cross-Linked Polyethylenes

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A reliable method is described for analyzing ultrahigh molar mass polyethylene (UHMW-PE) with a weight-average molar mass of 5700 kg/mol and molar mass fractions up to 50,000 kg/mol by size exclusion chromatography (SEC) without molecular degradation as was proved by comparison of on-line and off-line viscometry. The use of low-bleed SEC columns (PLgel 20 μm Mixed-A LS), especially designed for on-line light-scattering detectors, allowed SEC to be coupled to a low-angle laser light-scattering detector without a filter ahead of the light-scattering cell. With this procedure, molded specimens of UHMW-PE, which are used for medical implants, such as hip endoprostheses, containing various amounts of α-tocopherol as a biocompatible stabilizer, were investigated. Furthermore, the effect of sterilization of the samples by γ-irradiation (^{60}Co, 1.33 MeV, absorbed dose: 25 kGy) was studied with respect to the content of insoluble cross-linked material and the molar mass distribution of the soluble fraction.

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Keywords: Ultrahigh molar mass polyethylene (UHMW-PE); Size exclusion chromatography (SEC); Low-angle laser light scattering (LALLS); Viscometry; γ-Sterilization; α-Tocopherol

INTRODUCTION

Ultrahigh molar mass polyethylene (UMHW-PE) has been used for medical implants (e.g., cups in total hip endoprostheses) since the 1960s[1]. Damage of the polyethylene caused by in vivo oxidation[2,3] leads to molar mass degradation[4], and therefore to higher crystallinity[5] and brittleness of the material. Consequently, increasing UHMW-PE debris surrounding the implant[6] may cause permanent inflammation of the tissue. Several attempts to reduce the wear of UHMW-PE at articulating surfaces in orthopedic implants have been made in the past. A feasible way is stabilization against in vivo oxidation by the addition of a biocompatible stabilizer to the UHMW-PE, e.g., α-tocopherol[7,8].

Sterilization with γ-irradiation strongly influences the properties of the UHMW-PE cups. High-energy radiation generally causes two antagonistic processes, cross-linking and random scission of the polymer chains, of which one usually predominates over the other[9]; polyethylene is known to be one of the polymers that are preferably cross-linked.

Size exclusion chromatography (SEC) has been established as a useful method for determining changes in the molar mass distribution caused by degradation. Based on long-term experiences with SEC of polyolefins[10], especially ultrahigh molar mass polymers[11], the aim of this work was to study the influence of sintering and γ-sterilization on the molar mass distribution and cross-linking of UHMW-PE with varying amounts of α-tocopherol as an antioxidant.

Starting from the pure UHMW-PE powder containing different amounts of α-tocopherol, specimens were produced in the same way as for medical implants by sintering and sterilization with γ-radiation. In every step the samples were characterized with respect to their solubility and molar mass distribution of the soluble fraction.

EXPERIMENTAL

Materials

The UHMW-PE powder Hostalen® GUR 1020 (Lot B15331047) (Hoechst AG, Frankfurt/Main, Germany, commercially available from Ticona GmbH, Frankfurt, Germany, GUR® 1020) and α-tocopherol (Lot 606876) (Hoffmann-La Roche AG, Basel, Switzerland) were used. The UHMW-PE powder was homogeneously mixed with α-tocopherol

(0, 0.2, 0.4, and 0.8%, w/w) and was sintered for 7 h at 220°C and a pressure of 35 bar at Isosport GmbH, Eisenstadt, Austria.

A part of the sintered specimens were irradiated with γ-radiation (^{60}Co, 1.33 MeV, absorbed dose: 25 kGy) in a nitrogen atmosphere. This γ-sterilization was carried out at Sulzer Orthopedics Ltd. (Winterthur, Switzerland) according to its internal standard procedure.

An overview of all polyethylene samples as well as their corresponding polymer code used in this work is given in Table I.

The samples for the determination of the solubility and molar mass distribution were taken from microtome sections about 500 μm below the surface of the specimens.

Size Exclusion Chromatography (SEC)

The molar mass distribution of the UHMW-PE samples was determined at 135 ± 0.02°C with a GPC 220 chromatograph (Polymer Laboratories, Church Stretton, U.K.) equipped with a differential refractive index (DRI) detector (Polymer Laboratories), a differential viscometer 210 R (Viscotek, Houston, Tex., USA), and coupled with a low-angle laser light-scattering (LALLS) photometer KMX 6 ($\lambda = 633$ nm) (Chromatix, Sunnyvale, Calif., USA). A set of two columns was used, packed with cross-linked styrene-divinylbenzene (PLgel® Mixed-A LS, particle size: 20 μm, length: 300 mm, i.d.: 7.5 mm; Polymer Laboratories). The columns are "low-bleeding", especially designed for on-line light scattering detection. Therefore, no filter ahead of the light-scattering cell was needed, which causes degradation of ultrahigh molar mass samples[11]. The increment of the refractive index, *dn/dc*, was assumed to be −0.104 mL/g[12].

TABLE I Polyethylene samples investigated and corresponding polymer codes

Polymer code	Mass content of stabilizer (%)	γ-irradiated
[a]PE-0	0	no
[b]PE-0s	0	no
[b]PE-0.2s	0.2	no
[b]PE-0.4s	0.4	no
[b]PE-0.8s	0.8	no
[b]PE-0sγ	0	yes
[b]PE-0.2sγ	0.2	yes
[b]PE-0.4sγ	0.4	yes
[b]PE-0.8sγ	0.8	yes

[a] UHMW-PE powder.

[b] Sintered sample.

The compound 1,2,4-trichlorobenzene (Merck, Darmstadt, Germany) containing 0.0125% (w/v, mixed at 23℃) 2,6-di-*tert*-butyl-(4-methylphenol) (BHT) was used as solvent and as eluent after filtration through a 0.45 μm PTFE filter. Prior to entering the pump, it was degassed with an on-line degasser PL-DG2 (Erc Inc., Kawaguchi City, Japan). The flow rate was either 0.5 mL/min or, in the case of the ultrahigh molar mass samples, 0.2 mL/min to avoid molecular degradation[11]. The flow rate was continuously monitored with the aid of a flow meter (LiquiFlow, Bronkhorst, Netherlands) and its reproducibility was better than 99.8% for all flow rates selected.

The polymer solutions were prepared with amounts between 1 and 2 mg of the polymer in 10 mL of solvent and were flushed with nitrogen for 15 min at room temperature to avoid oxidative degradation during dissolution. The nitrogen was purified with the Oxisorb® gas-cleaning system (Linde AG, Höllriegelskreuth, Germany) and contained less than 0.0001% (v/v) oxygen. The samples were then placed in an oven and were rolled by a self-assembled apparatus at about 3 revolutions/min at 150℃ for 4 h prior to injection. This procedure homogenizes the samples with negligible mechanical stress and avoids oxidative degradation during SEC runs.

Viscometry

The off-line viscometry measurements were carried out with a "rolling-sphere capillary viscometer" AMV 200 (Anton Paar KG, Graz, Austria) at 135℃ in 1,2,4-trichlorobenzene containing 0.0125% (w/v) BHT. The capillary i.d. was 1.7 mm, the diameter of the stainless steel sphere was 1.5 mm, and the rolling angle selected was 40°.

Determination of the Insoluble Fraction

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

RESULTS AND DISCUSSION

As shown in our studies with polystyrene standards[11], ultrahigh molar mass polymers are degraded by mechanical forces during SEC. The degradation especially occurs inside filters and frits of the chromatographic system if high flow rates are applied. Therefore, for these experiments, special SEC columns were used that can be utilized without any filter ahead of the light-scattering cell, which usually is the most critical point of the system.

Compared to polystyrene in toluene[11], polyethylene in 1,2,4-trichlorobenzene has a larger molecular diameter, d_m, at the same molar mass (see Figure 1), which can be estimated assuming a spherical macromolecular shape in solution. On the basis of the Staudinger-Mark-Houwink equation $[\eta] = K \times M^a$ and the hydrodynamic volume $V_h \approx [\eta] \times M$, with $V_h = 4/3 \times \pi \times (d_m/2)^3$, the molecular diameter can be expressed by

$$d_m[\mu m] = 2 \times \left[3 \times K \times M^{a+1} \times 10^{12}/(4 \times \pi \times N_A)\right]^{1/3}$$

where M is molar mass (g/mol), N_A is Avogadro's number, $K = 1.069 \times 10^{-2}$ (mL/g) and $a = 0.724$ for polystyrene in toluene at 20℃[13], and $K = 4.06 \times 10^{-2}$ (mL/g) and $a = 0.725$ for polyethylene in 1,2,4-trichlorobenzene at 135℃[12].

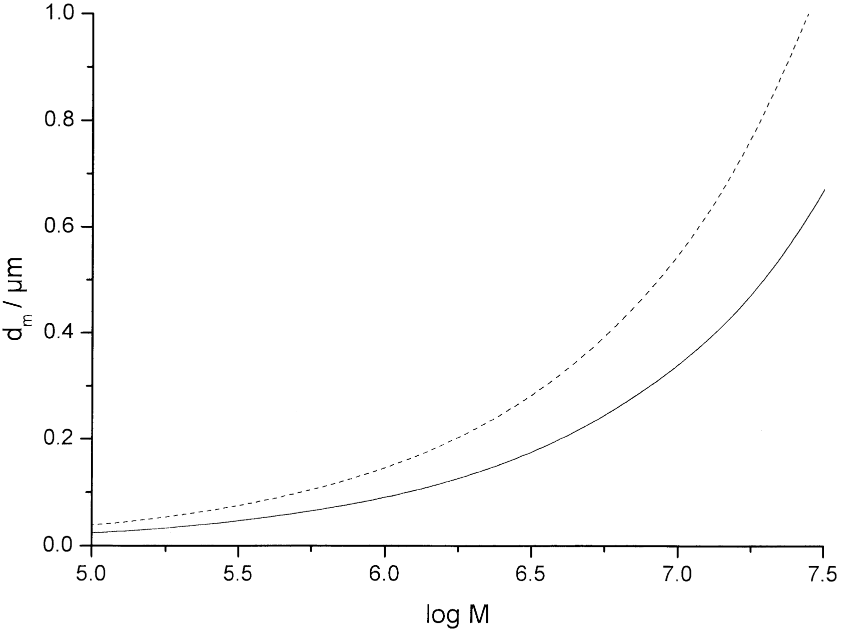

FIGURE 1 Calculated molecular diameters d_m for polystyrene in toluene at 20℃ (solid line) and polyethylene in 1,2,4-trichlorobenzene at 135℃ (dashed line) as a function of the molar mass M (see text).

The flow rate was reduced to 0.2 mL/min for measurements of all polyethylene samples containing ultrahigh molar mass fractions to avoid molecular degradation.

Figure 2 shows the tracings of the viscometer and the differential refractometer as a function of elution volume V_E of the UHMW-PE powder PE-0. The refractometer signal is proportional to the concentration, and the signal of the viscometer is proportional to the product of intrinsic viscosity and the concentration. By dividing the viscometer signal by the refractometer signal the intrinsic viscosity at each elution volume increment is obtained[14]. Integration of this function leads to the intrinsic viscosity of the total eluted polymer sample $[\eta]_{\text{total}}$.

The results from on-line viscometry determined by SEC show very good agreement with those derived from off-line viscometry, which indicates that under the applied conditions no molecular degradation of the polymer had occurred (Table II).

Figure 3 shows the elution curves and the light-scattering calibration curves of the UHMW-PE powder PE-0 and the sintered, unstabilized specimen PE-0s. The LALLS calibration curves are almost identical within the overlapping range of the elution curves. This indicates the

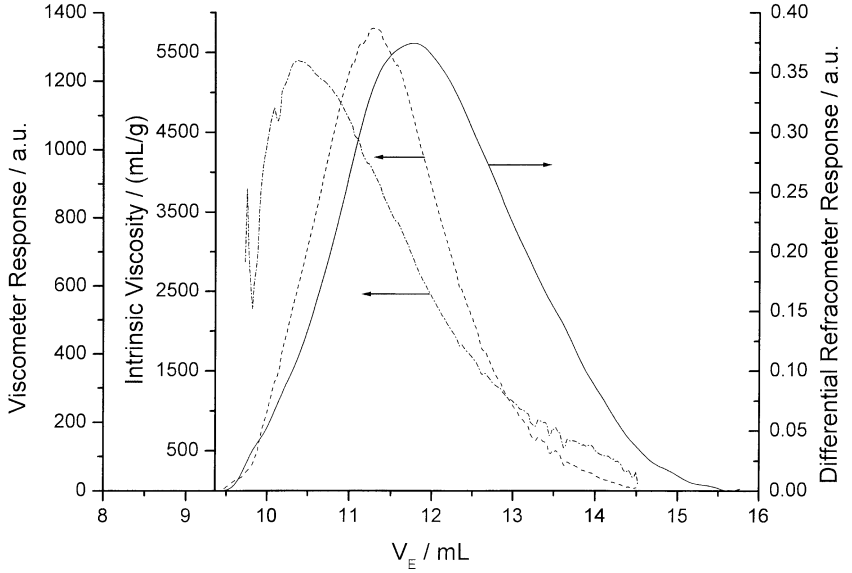

FIGURE 2 Concentration signal of the DRI detector (solid line) and signal of the viscometer (dashed line) as well as the intrinsic viscosity (dash-dotted line) as a function of the elution volume V_E of the UHMW-PE powder PE-0 (see text).

TABLE II Intrinsic viscosity derived from on-line viscometry, $[\eta]_{\mathrm{total}}$, (see text) and off-line viscometry $[\eta]_{\mathrm{offline}}$, measured with the "rolling-sphere capillary viscometer" of the soluble fraction of the UHMW-PE prior to and after sintering with various mass contents of α-tocopherol

Polymer code	$[\eta]_{\mathrm{total}}$ (mL/g)	$[\eta]_{\mathrm{offline}}$ (mL/g)
PE-0	2700	2650
PE-0s	1600	1650
PE-0.2s	1950	1970
PE-0.4s	1950	1950
PE-0.8s	1850	1820

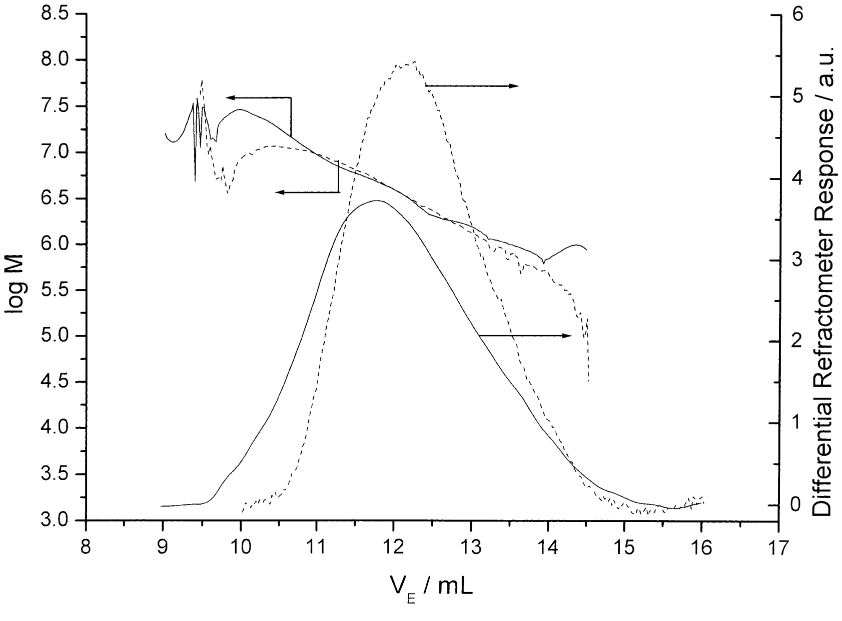

FIGURE 3 Concentration signal of the DRI detector and light-scattering calibration curves of the UHMW-PE powder PE-0 (solid line) and the soluble fraction of the sintered, unstabilized specimen PE-0s (dashed line).

absence of any major amount of branched material formed during the sintering process[15]. The corresponding molar mass distribution curves are depicted in Figure 4. The UHMW-PE powder PE-0 is completely soluble and contains molar mass fractions up to 50,000 kg/mol.

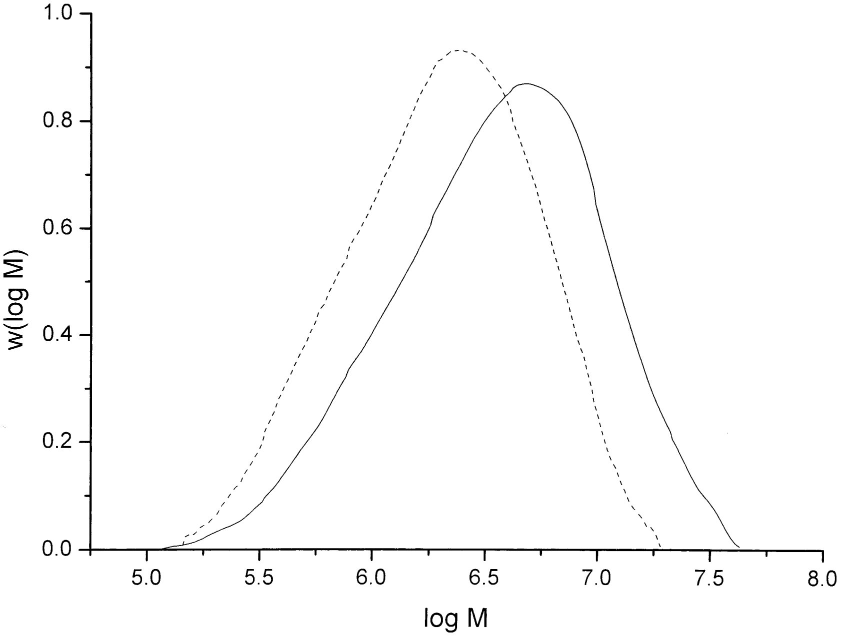

FIGURE 4 Molar mass distribution of the UHMW-PE powder PE-0 (solid line) and the soluble fraction of the sintered, unstabilized UHMW-PE, PE-0s (dashed line).

During the sintering process a significant change in solubility occurs. After the sintering process, the specimen made from the originally completely soluble UHMW-PE powder shows a mass fraction of insoluble gel of about 50% and the molar mass of the soluble fraction decreases (Table III). The dashed line in Figure 4 shows the molar mass distribution of the soluble fraction of unstabilized Hostalen® GUR 1020 after sintering, PE-0s. Apparently, the high molar mass fraction is affected preferably by cross-linking. The weight-average molar mass of the soluble fraction of the sintered sample drops to 2900 kg/mol and the highest molar mass fraction reaches a value of only $M_w \approx$ 20,000 kg/mol.

By adding stabilizer to the UHMW-PE prior to sintering, the insoluble fraction is reduced from 48 to 20% in the case of sample PE-0.8s, containing 0.8% α-tocopherol (Table III). The weight-average molar mass of the soluble fraction of the sintered UHMW-PE, PE-0s, increases from 2900 to 3800 kg/mol. The polydispersity PD ($PD = M_w/M_n$, M_n: number-average molar mass) of the soluble fraction of the sintered

TABLE III Mass content of the insoluble fraction, weight-average molar mass M_w, and polydispersity PD ($PD = M_w/M_n$) of the soluble fraction of the UHMW-PE prior to and after sintering with different mass contents of α-tocopherol as stabilizer

Polymer code	Insoluble fraction (%)	M_w (kg/mol)	PD
PE-0	0	5700	2.9
PE-0s	48	2900	2.3
PE-0.2s	28	3600	2.1
PE-0.4s	26	3600	2.2
PE-0.8s	20	3800	2.2

samples is close to 2, nearly independent of the content of stabilizer, suggesting that the soluble fraction of sintered UHMW-PE has undergone mainly a random scission process.

The sterilization process by γ-radiation completely changes the characteristics of the polymer. Table IV shows the dependency of the solubility and the molar mass of the soluble fraction on the concentration of α-tocopherol caused by the sterilization process of the sintered UHMW-PE with γ-radiation. The unstabilized sample PE-0sγ is cross-linked, leading to about 82% of an insoluble fraction, whereas the stabilized samples contain an insoluble fraction of only 60 to 65%. Apparently, the addition of α-tocopherol reduces cross-linking of irradiated polyethylene.

The stabilizer not only reduces cross-linking in the irradiated polyethylene, but also affects the antagonistic reaction to cross-linking, i.e., molecular degradation. Figure 5 shows the molar mass distribution curves of the soluble fractions of the irradiated unstabilized (PE-0sγ) and the stabilized UHMW-PE sample containing 0.8% α-tocopherol (PE-

TABLE IV Mass content of the insoluble fraction, weight-average molar mass M_w, and polydispersity PD ($PD = M_w/M_n$) of the soluble fraction of the sintered UHMW-PE samples with different mass contents of α-tocopherol as stabilizer after γ-irradiation (nitrogen atmosphere, ^{60}Co, 1.33 MeV, absorbed dosage 25 kGy)

Polymer code	Insoluble fraction (%)	M_w (kg/mol)	PD
PE-0sγ	82	370	2.0
PE-0.2sγ	65	680	1.8
PE-0.4sγ	62	695	1.8
PE-0.8sγ	60	730	1.7

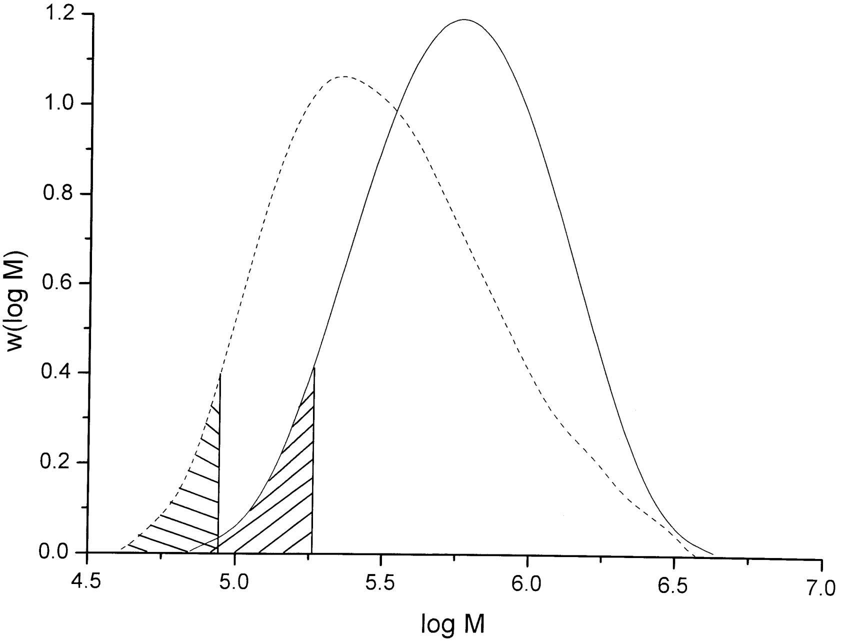

FIGURE 5 Molar mass distribution of the soluble fraction of the sintered UHMW-PE sample after γ-irradiation (nitrogen atmosphere, ^{60}Co, 1.33 MeV, absorbed dosage 25 kGy) without (dashed line) (PE-0sγ) and with 0.8% α-tocopherol (solid line) (PE-0.8sγ).

0.8sγ). The low molar mass fraction, which results from molecular degradation of larger molecules, indicates the stabilizing effect of the α-tocopherol. The weight-average molar mass of the lowest 10% of the molar mass distributions (dashed areas in Figure 5) of the unstabilized irradiated sample is 85 kg/mol, whereas that of the stabilized sample is 166 kg/mol. The low molar mass tail of the distribution of the unstabilized sample starts at 35 kg/mol and the one stabilized with 0.8% α-tocopherol starts at 70 kg/mol (Figure 5). Apparently, α-tocopherol also considerably reduces the molecular degradation of low-molar mass fractions caused by γ-radiation. The stabilizer reduces both molecular degradation and cross-linking. The stabilizer causes a slight reduction of the polydispersity of the soluble fraction, since it reduces the extent of molecular degradation of the low molar mass fractions and does not change the "cutoff" molar mass of the high molar mass range of the soluble fraction.

CONCLUSIONS

The methods that were developed to analyze ultrahigh molar mass polystyrene[11] are also suitable for UHMW-PE without any molecular degradation, as shown by comparative viscosity measurements.

UHMW-PE undergoes cross-linking reactions during sintering and γ-sterilization. The compound α-tocopherol was shown to be an efficient radical scavenger, which can partially prevent UHMW-PE from being degraded during sintering and irradiation with high-energy radiation, and also reduces the extent of cross-linking.

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