Thermal stability and degradation of hydrocarbon metathesis polymers

A. Mühlebach [a,*], P.A. van der Schaaf [a], A. Hafner [a], F. Setiabudi [b]

[a] *Additives Research, Ciba Specialty Chemicals, 1723 Marly, Switzerland*
[b] *Performance Polymers Research, Ciba Specialty Chemicals, 4002 Basel, Switzerland*

Abstract

The thermal stability of poly(dicyclopentadiene), made with $RuCl_2(p\text{-cymene})(PCy_3)$ as initiator, was investigated by ageing 2 and 5 mm plates up to 1 year at 180°C in air, or 360 h in a weather-o-meter. The surface roughness and microhardness of unstabilized and stabilized (0.1% Irganox[®] 1520, 0.5% Tinuvin[®] 171) probes were determined. Stabilization leads to an overall softer material but with a harder surface oxide layer with finer cracks, limiting the oxygen diffusion rate into the material and therefore protecting the underlaying material from fast oxidation. This is further supported by chemiluminescence (CL) measurements of 50 and 150 μm films of poly(DCPD) under strong oxidative conditions (150°C in pure O_2). It was found that even the unstabilized material is extremely resistant to oxidation, far superior to saturated poly(α-olefins) like poly(propylene). Pyrolysis of poly(DCPD) and poly(cyclooctene) (Vestenamer[®]) at 670°C under an inert atmosphere gave mixtures of cyclic and open-chain unsaturated hydrocarbons. Surprisingly, the pyrolysis of poly(norbornene) (Norsorex[®]) gives squalene in $>90\%$ yield. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: ROMP; Poly(dcpd); Thermal stability; Stabilizers; Squalene; Ru-catalysts

1. Introduction

Dicyclopentadiene (DCPD) is a very cheap and good available strained cyclic olefin. Poly(DCPD), obtained by ring-opening metathesis polymerization (ROMP), shows a unique combination of excellent physical and electrical properties (e.g. high impact strength, *E*-modulus, heat distortion temperature, low water absorption, etc.), far superior to most other thermoplasts and thermosets currently available on the market [1,2]. However, because of the high unsaturation of the polymer backbone, oxygen and especially ozone may have a detrimental effect on the polymer properties. Although a hard oxide layer limits the oxygen diffusion rate into the material and protects the underlaying material from fast oxidation [3,4], efficient stabilizers against long term thermal and light induced oxidation may be needed.

Our goal was to investigate the thermooxidative stability of plates and films of poly(DCPD), made with a ruthenium catalyst, by ageing them

* Corresponding author. Tel.: +41-26-4356520; fax: +41-26-4356219; e-mail: andreas.muehlebach@chma.mhs.ciba.com

at 150–180°C in air or O$_2$ and in a weather-o-meter. Physical and electrical properties, surface roughness, microhardness and chemilumines-cence (CL) results of unstabilized and stabilized probes were compared after different time intervals (up to 1 year). Furthermore, we investigated the thermal stability of some hydrocarbon ROMP polymers and identified their most important pyrolysis products.

2. Experimental

2.1. Starting materials

DCPD (94%, technical grade) was obtained from Shell, degassed and stored over molecular sieves.

Plates of poly(DCPD) (2 and 5 mm) were obtained by dissolving 0.3–0.5 wt% RuCl$_2$(p-cymene)(PCy$_3$) [5] in DCPD, adding additives and/or fillers, pouring this solution into steel moulds and subsequent curing in an oven 1 h at 80°C, 1 h at 100°C and 2 h at 120°C [6,7]. Properties: T_g, 120°C and swelling in toluene, 100%. 50–150 μm thick sections from this plate were cut with a hard metal knife micro-tome for CL-measurements. Poly(cyclooctene) (Vestenamer® 6213, Hüls AG) and poly(norbornene) (Norsorex® N, Nippon Zeon) were used as received. The standard epoxy resin used in the studies described below was a bisphenol F based epoxy resin (Araldite® GY 281) cured with a liquid anhydride hardener (Araldite® HY 906) and an accelerator Aral-dite® DY 062), all commercial products from Ciba SC. The stabilizers Irganox®1520 and

Tinuvin® 171 are also commercial products from Ciba SC, see Fig. 1.

2.2. Measurements

The pyrolysis experiments were done at 670°C on a Fischer Curie Point-Pyrolyzer and GC-MS analysis was performed on a Hewlett-Packard Model 5890 followed by a SSQ 710 from Finnigan MAT. The mass spectra were compared with reference data from the Masslib Siscom-Search (Wiley-Library). A CL imaging apparatus based on a cryogenically cooled, slow scan CCD camera [8] was used to study the thermal oxidation of poly(DCPD). The surface profile was characterized by a Form Talysurf S3C-50 in 2D-mode, the surface hardness mea-sured by Fischerscope H100 with a Vickers diamond indentor.

3. Results and discussion

3.1. Ageing experiments

To study the change in mechanical and elec-trical properties as well as the influence of stabilizers on the stability of plates of poly(DCPD), oven ageing and ageing experi-ments in a weather-o-meter were carried out. Fig. 2 shows the oven ageing in air of unstabi-lized 5 mm poly(DCPD) plates, compared with the standard epoxy resin.

In contrast to the epoxy plate, the poly(DCPD) plate shows almost no weight loss up to 100 days of ageing at 180°C in air. However, the weight loss increases rapidly thereafter, reaching almost 12% after 300 days. The glass transition temperature (T_g) increased dramatically from 120 to 195°C within the first 28 days, whereas the swelling in toluene de-creases from 100 to 42%. This strongly suggest that during the ageing experiment the crosslink density has increased. Surprisingly, the E-mod-ulus has not changed significantly during the first 28 days of ageing. Also the electrical prop-
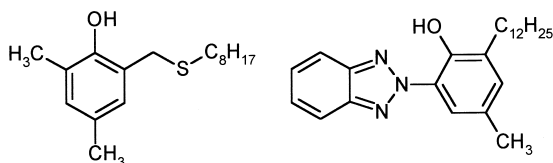

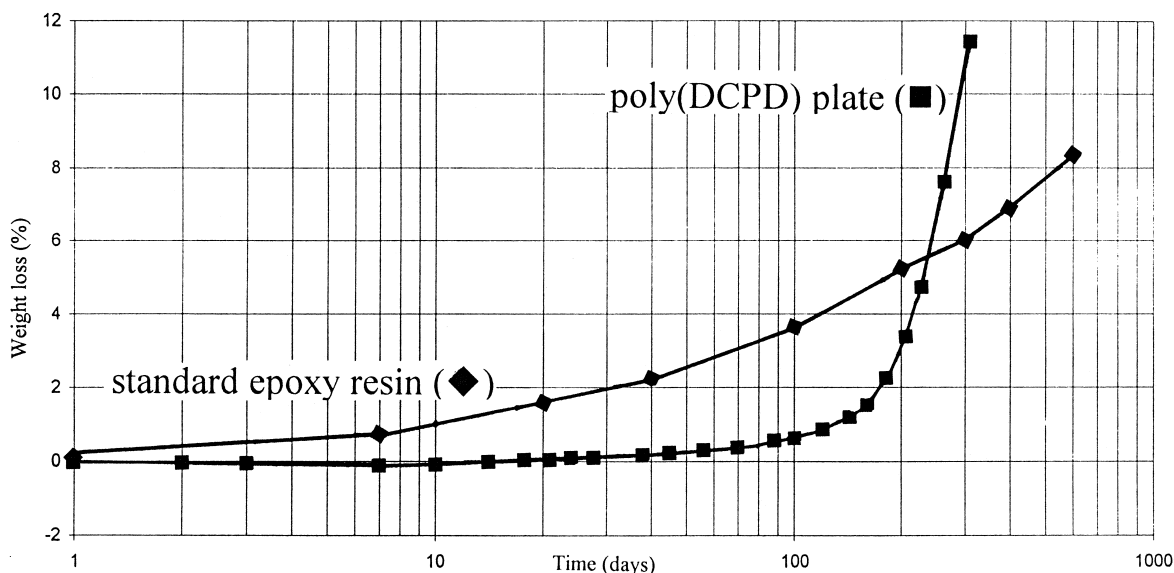Fig. 1. Structures of Irganox® 1520 (left) and Tinuvin® 171 (right).

Fig. 2. Oven ageing of a 5 mm poly(DCPD) plate. Weight loss (%) versus storage time (days, logarithmic scale) at 180°C in air, compared with a standard epoxy resin.

erties (ε and tan δ at 50 Hz) did not change during this time period.

To investigate the influence of stabilizers on poly(DCPD), 2 mm plates with 0.1% Irganox[®] 1520 and 0.5% Tinuvin[®] 171 were aged at 60°C for 360 h in a weather-o-meter and compared with unstabilized probes aged under the same conditions. Since the color change gave no clear indication on the extent of the oxidative degradation, surface roughness and surface hardness measurements were performed. As expected, the roughness and crack depth increases with ageing and stabilization leads to a finer and less deep crack structure, see Fig. 3.

For both, the stabilized and unstabilized sample, the surface hardness is about 1.5 times higher than the hardness in 4.5 μm depth. The values are lower in the stabilized sample, most probably due to a negative influence of the stabilizers on the catalytic curing reaction. However, another possibility could be the formation of oxidation bridges between polymer chains on the surface in the unstabilized sample. This difference between the surface hardness and the hardness in ca. 4.5 μm depth increases during ageing to a factor of 2 for the unstabi-

lized and a factor of almost 3 for the stabilized sample. The stabilizing effect of Irganox 1520 and Tinuvin 171 is therefore indirect because stabilization leads to a softer material. This softening facilitates O_2-permeation and therefore leads to a harder surface layer, which protects the underlaying material from further oxidation (Fig. 4)!

3.2. Chemiluminescence (CL) and UV-microspectrometry measurements on poly(DCPD) films

To study the speed of oxidation and the influence of the presence of stabilizers in films of poly(DCPD), we performed some chemiluminescence (CL) measurements [8]. Fig. 5 shows the results of these measurements for poly(DCPD) films of 50 and 150 μm, stored at 150°C under a O_2- or N_2-flux (250 ml/min).

The first observation which can be made from these CL-images is that all samples gave rise to only a weak CL-signal (an identical polypropylene sample emits ca. 20 times more photons!). Secondly, the CL-intensity reaches a
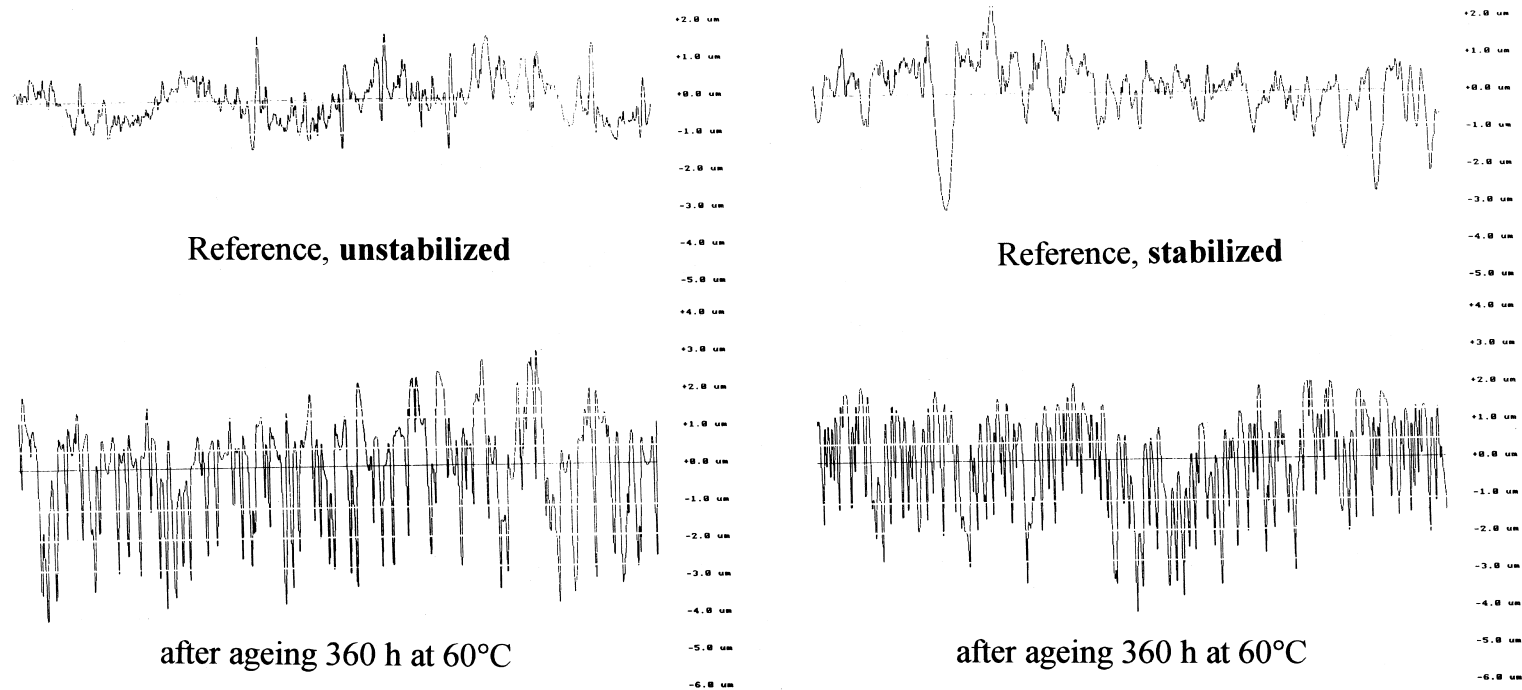
Reference, **unstabilized**

Reference, **stabilized**

after ageing 360 h at 60°C

after ageing 360 h at 60°C

Fig. 3. Surface profile of unstabilized and stabilized poly(DCPD) plates before and after ageing in a weather-o-meter.

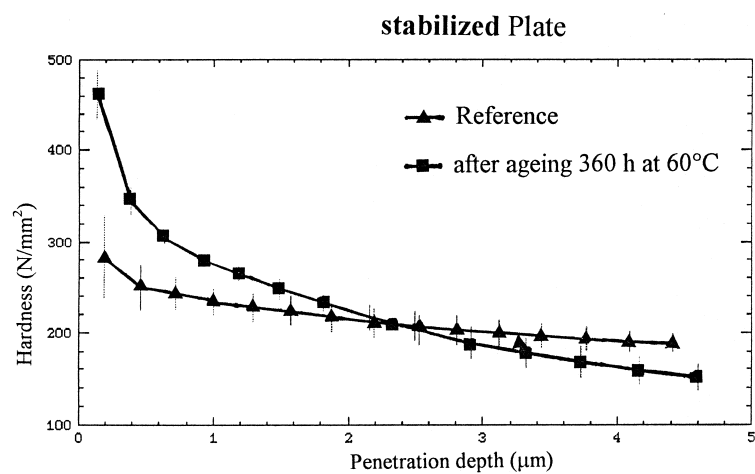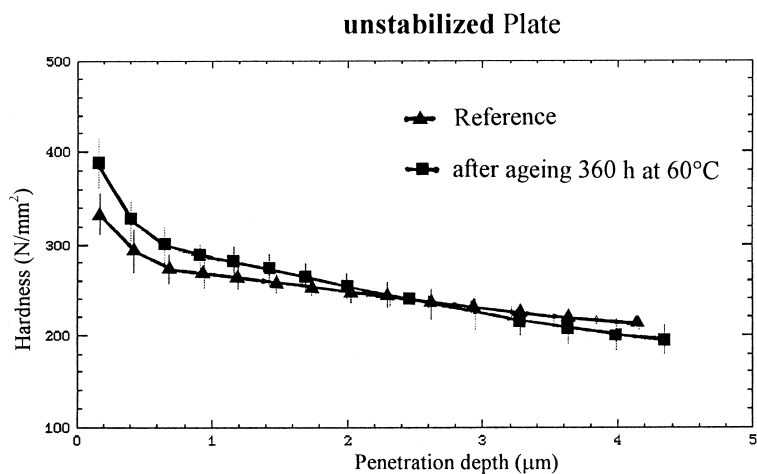**unstabilized Plate**   **stabilized Plate**

Fig. 4. Hardness measurements (surface to 4.5 μm depth) of unstabilized and stabilized poly(DCPD) plates before and after ageing in a weather-o-meter.
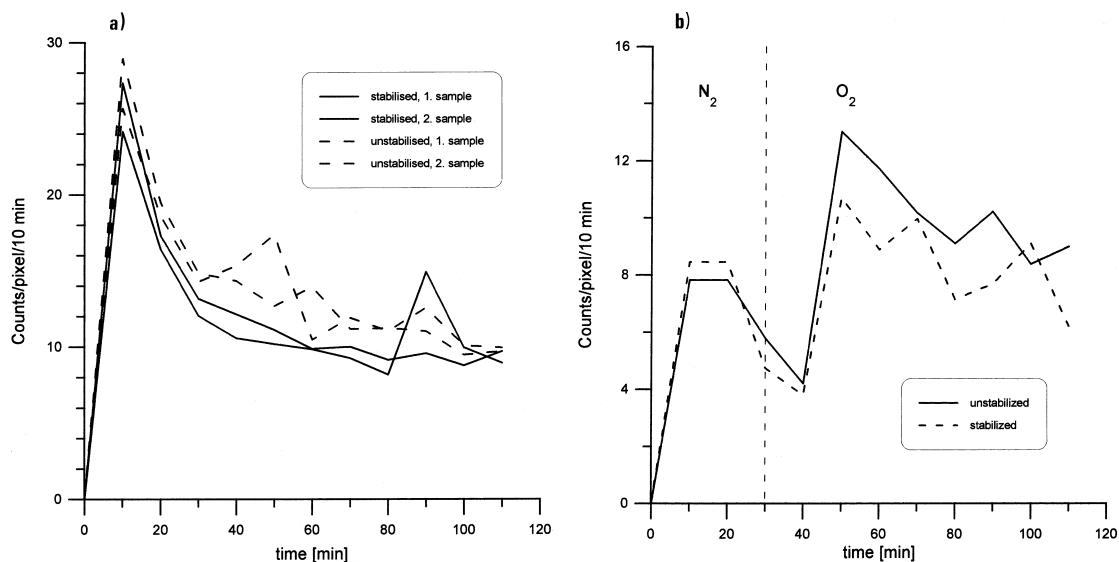
Fig. 5. CL-measurements of poly(DCPD) films at 150°C. (a) Film thickness: 150 μm, pure O_2 and (b) film thickness: 50 μm, 30 min in N_2, than pure O_2.

maximum after 10 min and than decreases drastically to a very low level. Thirdly, there are no significant difference observed between the unstabilised and the stabilized samples. Again, as concluded from the ageing experiments, the material is well 'self-stabilized' towards oxidation and therefore the influence of both stabilizers is small.
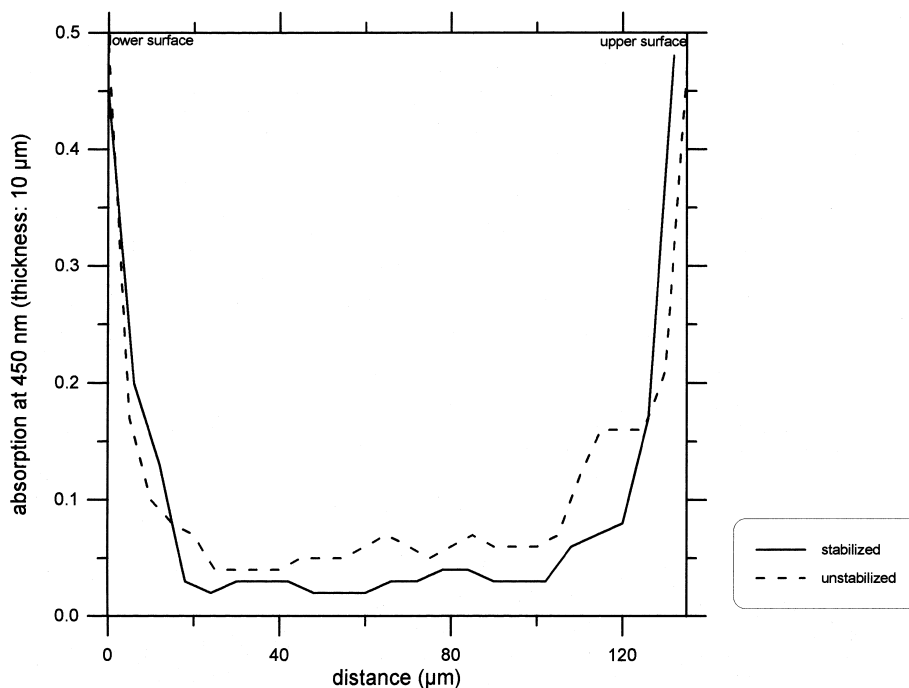

Fig. 6. UV-microspectrometric measurement of a ca. 140 μm thick film of poly(DCPD), aged at 150°C for 2 h. Absorption at 450 nm versus distance from both surfaces (cut thickness: 10 μm).

With UV-microspectrometry we investigated the UV-absorption over the whole sample thickness of 150 μm thick poly(DCPD) films aged at 150°C for 2 h.

Fig. 6 shows that the absorption at 450 nm is highest on both surfaces and decreases sharply and symmetrically within the first 20 μm. Both CL and UV-microspectrometry measurements strongly indicate that the diffusion of O_2 into the sample is the limiting factor in the oxidation of poly(DCPD).

3.3. Pyrolysis

The thermal stability of the three hydrocarbon metathesis polymers of norbornene, cyclooctene and DCPD were studied by pyrolysis experiments at 670°C and GC-MS analysis. Poly(cyclooctene) decomposes into a mixture of low molecular weight aliphatic hydrocarbons ($\leq C_8$). The main product of the pyrolysis of poly(DCPD) is cyclopentadiene (70%) which, in principle, is the product of a clean depolymerization. The remaining pyrolysis products of poly(DCPD) are, besides cyclohexadiene, a mixture of aromates, like toluene, (methyl)indane, (methyl)indene and (methyl)-dihydro- and tetrahydro-naphthalene. Surprisingly, the pyrolysis of poly(norbornene) gave squalene ((2,6,10,15,19,23 - hexamethyl) -2,6,10,14,18,22-etracosahexaene) in an almost quantitative yield, see Fig. 7. Squalene, a natural product extracted from deep sea shark's liver oil, is used, for example, as food supplement to strengthen the immune system and in skin creams to prevent altering. The mechanism of this bizarre transformation is not clear to us yet.
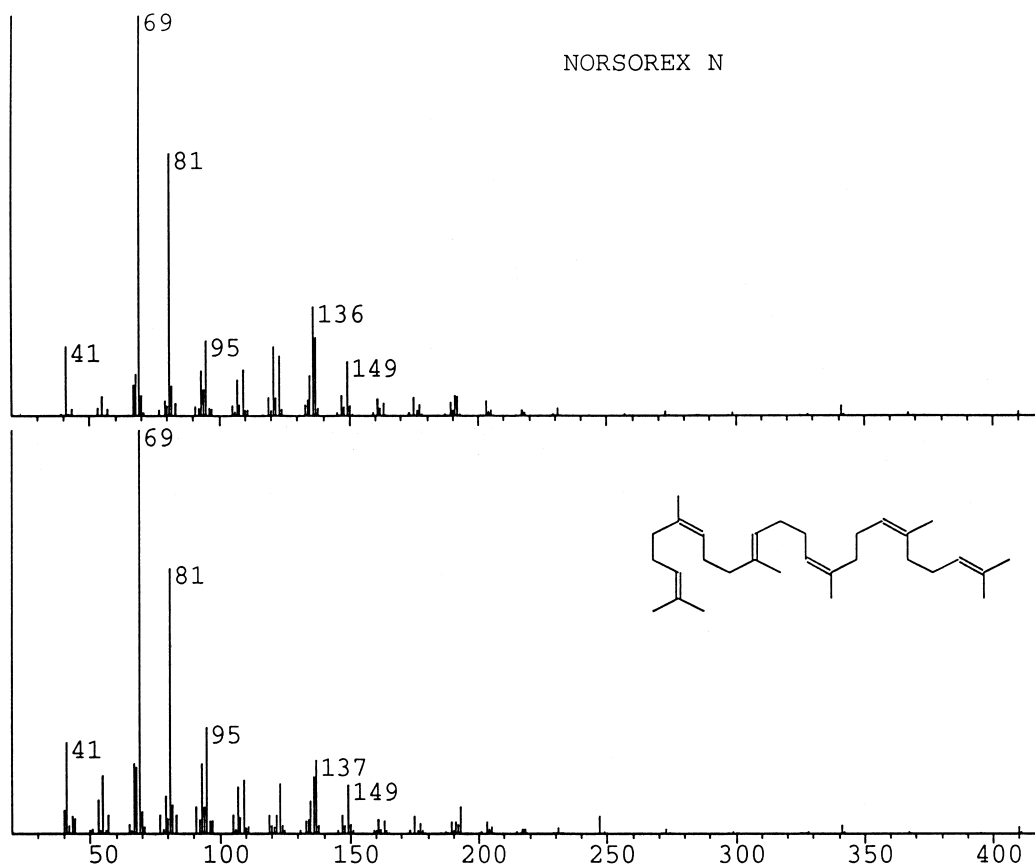

Fig. 7. MS-trace (m/E) of pyrolized Norsorex ® N (above) compared with commercial squalene (below).

4. Conclusions

Due to the dense and hard surface oxide layer which limits efficiently the oxygen diffusion rate into the material, the oxidative stability of poly(DCPD) plates is indeed remarkable. The thickness of this layer was measured to be between ca. 4–20 μm, depending strongly on the ageing conditions. Stabilization with ordinary antioxidants and UV-absorbers leads to an overall softer material forming upon oxidation an even thicker and harder surface layer.

Whereas the pyrolysis of most ROMP polymers leads to mixtures of aliphatic and aromatic hydrocarbons, poly(norbornene) gives squalene, a natural product, in good yield.

References

[1] S.M. Doughty, G. Recher, Y.S. Yang, Kunststoffe 82 (1996) 1191.
[2] S.M. Doughty, G. Recher, Y.S. Yang, Kunststoffe 86 (1996) 11.
[3] S. Mallet, B. Chartier, M. Autran, P. Moreau, B. Mortaigne, 11th IUPAC/FECS International Conference on Polymers, Bratislava, 24–28 June 1996, poster abstract.
[4] Y.S. Yang, E. Lafontaine, B. Mortaigne, J. Appl. Polym. Sci. 60 (1996) 2419.
[5] M.A. Bennett, A.K. Smith, J. Chem. Soc. Dalton Trans. (1974) 233.
[6] A. Hafner, P.A. van der Schaaf, A. Mühlebach, WO 96/20235, Ciba SC, prio. 23.12.94.
[7] A. Hafner, A. Mühlebach, P.A. van der Schaaf, Angew. Chemie 109 (1997) 2213 (Angew. Chem. Int. Ed. Engl. 36 (1997) 2121).
[8] D.J. Lacey, V. Dudler, Polymer Degrad. Stability 51 (1996) 101.