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Peroxide-initiated grafting of maleimides onto hydrocarbon substrates

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Abstract

The grafting of *N*-phenethyl-maleimide (**1**) onto squalane and eicosane was investigated. As reference substances for spectroscopical investigations homopolymer, *N*-phenethyl-succinimide (**2**), *t*-butyl-(**4**) and cyclohexyl-*N*-phenethyl-succinimide (**6**) were synthesized. The grafting reactions were carried out at 150 °C in 1,2-dichlorobenzene with Luperox 130 as initiator (molar ratio hydrocarbon substrate:**1**:initiator = 10:1:0.2). Two fractions of graft products were isolated and analysed by ^{1}H NMR, ^{13}C NMR, FTIR and UV spectroscopy, SEC and MALDI-TOF MS to determine the average number of grafted residues per substrate molecule and to elucidate the structure of the grafts and the grafting sites. Overall grafting yields were found to be >90%. Only a small percentage of the total amount of substrate was grafted (2–3%). First fraction of both oligomers (approx. 25 wt%) showed to be a mixture of homopolymers (average degree of polymerization 6) and graft products (approx. 1:3), the latter containing mainly long-chain grafts with an average chain length of 7. The major fraction of graft products contained predominantly single units. As an average number of units per substrate molecule very similar results were obtained for eicosane and squalane ($n = \sim 3$). In the case of squalane single units were found to be linked mainly to tertiary carbon atoms, long chain grafts mainly to secondary C-atoms. Apart from the homopolymers resulting from radical transfer, homopolymers terminated with methyl groups resulting from secondary radicals formed by the decomposition of Luperox were also observed. Homopolymers as well as graft products were found to contain small amounts of maleimide groups. The results suggest that as in the mechanism proposed for maleic anhydride, both inter- and intramolecular hydrogen abstraction occurs as part of the chain process. Termination proceeds mainly by hydrogen transfer and also by disproportionation, to a lesser extent. The formation of long chain grafts on tertiary carbons seems to be sterically hindered.

Keywords: Free radical grafting; Maleimides; Hydrocarbons; Model compounds; NMR spectroscopy; MALDI-TOF MS

1. Introduction

The free-radical-initiated functionalization of polyolefins has received considerable attention in recent years and has become a method largely used from an industrial point of view. Grafting is preferably

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performed in the melt, but routes via solution, solid state or vapour phase (surface modification) are known and/or have been applied. Such modifications yield single monomer grafts or short length grafts, changing substantially the polymer's reactivity and chemical and mechanical properties. The applications of modified polyolefins are usually based on the enhancement of adhesion between apolar polyolefins and polar substrates (polyamides, polyesters, coatings, glass, inorganics, metals, and paper) either on the macroscopic level (co-extrusion, over-moulding and adhesives) or on the microscopic level (compatibilizer and coupling agent) [1]. The performance of graft-modified polymers in adhesion and compatibilization as well as the mechanical properties can be expected to depend on the chemical microstructure of the graft, and thus a detailed study of it is important in understanding the structure–property relationships for these systems. Microstructure refers to features such as the site of the graft attachment (primary, secondary, tertiary sites) in the case of polyolefin substrates. In addition to the site of attachment, the issue of graft type (i.e., single, oligomeric, polymeric, bridging, and/or unsaturated) is also of interest. A detailed characterization of graft-modified polyolefins is very difficult due to the low levels of graft modification normally achieved. This makes the grafted product poorly sensitive to routine spectroscopic methods unless suitable methods for labeling the desired structural feature are available. These problems can be overcome by using low-molecular weight compounds such as for example dodecane, *n*-eicosane, isooctane or 2,6,10,15,19,23-hexamethyltetracosane (squalane) as model substrates for the grafting reaction. The structure of the grafts to these model compounds are more readily determined, and it is expected that the grafts in polyolefins will have similar structures [2].

As far as the grafting mechanism is concerned, it is generally accepted that the primary steps are: decomposition of the initiator, hydrogen abstraction from the polymer backbone, and reaction of the macroradical with a monomer molecule to form a branched macroradical. This branched macroradical may continue to react with more monomer molecules forming longer grafts. It may also undergo transfer with a hydrogen atom of the same or another polymer backbone forming a new macroradical and a graft consisting of a single monomer unit. As initiator, dialkyl peroxides are most commonly used. The decomposition mechanism of dialkyl peroxides is well established and involves initial O–O bond homolysis to generate the corresponding alkoxy radicals. Addition of alkoxy radicals to the grafting monomer, which would lead to homopolymers as undesired by-products, usually can be neglected, but alkyl radicals formed by decomposition of the primary radicals are known to preferably add to the monomer. Under typical grafting conditions, i.e. high temperature and low monomer concentration, the kinetic chain length for homopolymerization is much lower than in typical vinyl polymerizations and degrees of polymerization are relatively low [2]. With a few common vinyl monomers, there is a further restriction of chain growth due to low ceiling temperatures. Relatively high molecular weight homopolymers may be obtained if the monomer is not completely soluble in the hydrocarbon substrate due to homopolymerization of pure monomer in undissolved monomer droplets. It is generally accepted that crosslinking in PE and chain scission in PP may occur simultaneously with the graft reaction. With low molecular weight hydrocarbons in the presence of monomer such reactions are usually not observed. Only in a study of Drillieres et al. [3] of grafting (meth)acrylates onto squalane simultaneous grafting and β-scission of squalane was reported.

With a history of more than 20 years, the free radical-induced grafting of maleic anhydride (MA) onto polyolefin substrates is one of the most studied reactions of polyolefin modification processes [4]. With respect to the molecular structure of MA-grafted polyolefins, many suggestions have been made in the literature, but few of them have been experimentally proven. In hydrocarbon substrates there may be several different types of hydrogen atoms which are susceptible to free-radical attack. In the case of statistical ethylene–propylene copolymers the products from abstraction of both methine and methylene hydrogens were observed. With alternating ethylene–propylene copolymers and low molecular weight hydrocarbons such as squalane and 2,6,10,14-tetramethylpentadecane almost all the grafts were found to be attached to tertiary carbon atoms [2]. In a study of of MA-*g*-PP by ^{13}C NMR, Heinen et al. [5,6] found only the product from methine abstraction, and it was suggested that, if secondary or tertiary radicals are produced, they are transformed into the more stable tertiary radicals by subsequent inter- or intramolecular abstraction reactions. Only monomeric MA grafts have been demonstrated with the exception of PE grafted in the melt:mixtures of monomeric, dimeric and trimeric grafts are then formed. Saturated MA grafts have been observed, with the exception of PP, where terminal grafts with an exo-cyclic unsaturation are formed as a result of PP chain degradation at a tertiary MA graft site. Very recently a study by Yang et al. [7] of grafting [2,3-$^{13}C_2$] onto PE in solution revealed few oligo-MA grafts with a terminal unsaturated MA ring as well as more oligomeric grafts consisting of only saturated succinic anhydride rings formed by termination via disproportionation as well as hydrogen abstraction of a grafting radical. In a study by Ranganathan et al. [8], who investigated the influence of ester groups in the substrate by grafting [2,3-$^{13}C_2$]–MA to model esters such as methyl decanoate and methyl 2-hexylhexanoate, evidence for the formation of few single unsaturated grafts was found. MS on MA-grafted alkanes used as representative low-molecular weight models showed the presence of relatively large amounts of products with 2, 3 and even 4 single succinic anhydride grafts per alkane molecule [8,9]. Such multiple graft structures suggest the occurrence of intramolecular H-transfer.

Apart from MA, which has been intensively studied, a wide range of other monomers have been successfully grafted [2,4,10]. The use of dialkyl maleates has been advocated over MA due to their lower volatility, lower toxicity and greater solubility in the polyolefin melt. However, the maleate esters are significantly less reactive towards free radical addition than MA and grafting yields are generally lower. Moreover, the modification of polyolefins with vinylsilanes and various (meth)acrylic monomers has been widely studied. Most studies of (meth)acrylates deal with functional monomers. Contrary to MA, maleate esters and vinyl silanes, which are known to be reluctant to undergo homopolymerization, grafting of (meth)acrylates is complicated by concurrent homopolymerization, the extent of which depends markedly on grafting temperature and monomer concentration [2,4].

Despite the suitability of maleimides for grafting reactions due to a very low inherent susceptibility to homopolymerization under melt-processing conditions, resulting in very high grafting yields, and to the possibility of introducing a broad range of functionalities into the molecular structure without a decrease of reactivity as in the case of maleic acid esters, this substance class has been scarcely considered in the literature up to now [10–17]. In earlier work of our group [14] the insufficient solubility of aromatic maleimides in the polymer melt was found to be the main problem restricting grafting yields at higher monomer concentrations. Therefore, we focused on aliphatic maleimides and introduced a long-chain aliphatic spacer into the molecular structure to increase the solubility of monomers in the polymer melt. Grafting of an aspartic acid based aliphatic maleimide (0.25–4 wt%) onto PP in an extruder afforded grafting yields of 80–95% [15]. Until now the microstructure of grafts of aliphatic maleimides has only been investigated by Lee and Russel [18]. In this study *N*-methyl-maleimide was grafted onto eicosane and squalane and the precipitable fraction of the reaction mixture was analysed by ^{1}H NMR spectroscopy and elemental analysis. 5–8 units per substrate molecule were found to be grafted and it was concluded that, similar to MA, the grafts consisted of single *N*-methylsuccinimide units. In the present work, peroxide-initiated grafting of *N*-phenethyl-maleimide (**1**) onto the low-molecular weight hydrocarbons squalane and *n*-eicosane has been studied as model system for the melt-grafting of aliphatic maleimides onto polyolefins. Grafting was carried out in solution at elevated temperature with 2,5-dimethyl-2,5-di-(*tert*-butylperoxy)-hex-3-yne (Luperox) as initiator. In this article, the synthesis of several reference substances for spectroscopical analysis and first results of the structure analysis of graft products by ^{1}H and ^{13}C NMR, FTIR, UV spectroscopy, SEC and MALDI-TOF MS are reported.

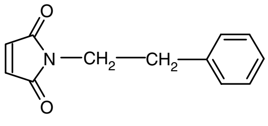
2. Experimental

2.1. Materials

Squalane (Sigma Aldrich), eicosane (Fluka), maleic acid anhydride (Loba Chemie), phenylethylamine (Aldrich), hexamethyldisilazane (Fluka), zinc bromide (Fluka), succinic anhydride (Merck), mercuric(II)chloride (Aldrich), *t*-butyllithium (Aldrich), sodium borohydride (Merck), cyclohexyl chloride (Merck) and magnesium turnings (Merck) were used as received. Analytical grade *o*-dichlorobenzene (Acros) was dried and distilled before use. All solvents (Donau Chemie and Müller-Scherr) were distilled before use. Column chromatography was performed with Merck silica gel 60 (0.063–0.200 mm). Thin-layer chromatography (TLC) was performed with Alugram Sil G/UV 254 sheets (Marcherey-Nagel). Luperox 130 [2,5-dimethyl-2,5-di-(*tert*-butylperoxy)-hex-3-yne ($t_{1/2} = 45$ min at 150 °C [4]) was received as a gift from Elf Atochem and used as provided.

2.2. Syntheses

N-phenethyl-maleimide (**1**) and *N*-phenethyl-succinimide (**2**) (Fig. 1) were synthesized according to the literature [19] in a one-step procedure by reaction of maleic anhydride and succinic anhydride, respectively, with phenylethylamine in the presence of hexamethyldisilazane and zinc bromide and purified by recrystallization from *n*-hexane (yield **1**: 75%, yield **2**: 78%). *t*-Butylmercuric chloride (**3**) was obtained by reaction of mercuric chloride with *t*-buthyllithium as reported in the literature [20] (yield 16%). Cyclohexylmercuric chloride (**5**) was synthesized by reaction of mercuric chloride with a Grignard-solution produced from cyclohexyl chloride and magnesium [21] (yield 65%). **3** and **5** were reacted with **1** to give the novel alkyl succinimides **4** and **6** (Fig. 2).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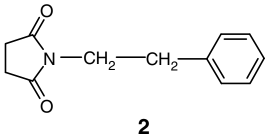
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Fig. 1. Structures of monomer **1** and reference compound **2**.

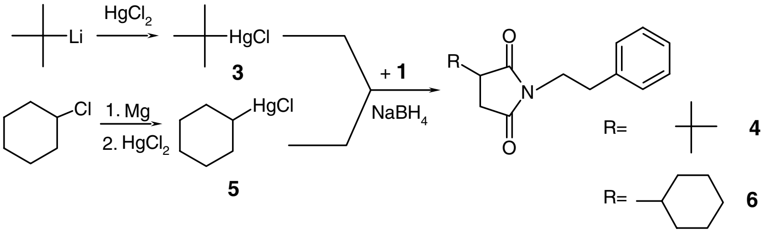

Fig. 2. Synthetic procedures for the preparation of reference compounds **4** and **6**.

*2.2.1. t-Butyl-N-phenethyl-succinimide (**4**)*

To a stirred solution of **1** (0.48 g, 2.4 mmol) and **3** (0.91 g, 3.1 mmol) in methylene chloride (10 mL) sodium borohydride (0.19 g, 5 mmol) was added at room temperature. After 10 min an exothermic reaction was initiated by adding water (0.5 mL). The mixture was stirred for 10 min and filtered through Florasil to remove excess water, mercury and solid byproducts. The solution was concentrated in vacuum. The crude product was purified by column chromatography (4:1 petroleum ether/ethyl acetate), $R_f = 0.50$).

Yield: 0.35 g (56%) white crystals; melting point: 74–75 °C; ^{1}H NMR ($CDCl_3$, δ, ppm): 7.38–7.09 (m, 5H, H–Ar), 3.77 (t, 2H, –*N*–CH_2–), 2.90 (t, 2H, –Ar–CH_2–), 2.68 (t, 1H, –CH–), 2.64–2.37 (m, 2H, –CH_2–), 1.00 (s, –9H, CH_3); ^{13}C NMR ($CDCl_3$, δ, ppm): 178.41 (C=O), 174.47 (C=O), 137.79 (C–Ar), 128.77 (C–Ar), 128.38 (C–Ar), 126.54 (C–Ar), 49.39 (–CH-succ), 39.47 (–N–CH_2–), 33.38 (Ar–CH_2–), 33.09 (–$\underline{C}$–CH_3), 31.48 (–CH_2-succ), 26.99 (–CH_3); IR (KBr): ν cm^{-1}: 2945, 1765, 1696, 1349, 1255, 1026, 880, 753, 701.

*2.2.2. Cyclohexyl-N-phenethyl-succinimide (**6**)*

6 was synthesized from **5** and **1** using the procedure described for **4** and was purified by column chromatography (4:1 petroleum ether/ethyl acetate), $R_f = 0.50$).

Yield: 0.40 g (57%) white crystals; melting point: 36–37 °C; ^{1}H NMR ($CDCl_3$, δ, ppm): 7.38–7.15 (m, 5H, H–Ar), 3.76 (t, 2H, –*N*–CH_2–), 2.91 (t, 2H, –Ar–CH_2–), 2.69 (t, 1H, –CH–), 2.63–2.33 (m, 2H, –CH_2–), 2.03–1.47 (m, 5H –CH_2–, –CH–), 1.41–0.86 47 (m, 6H –CH_2–); ^{13}C NMR ($CDCl_3$, δ, ppm): 179.06 (C=O), 176.77 (C=O), 137.62 (C–Ar), 128.80 (C–Ar), 128.39 (C–Ar), 126.51 (C–Ar), 45.16 (–CH-succ), 39.58 (–*N*–CH_2–), 38.52 (–CH–) 33.41 (Ar–CH_2–), 30.83 (–CH_2-succ), 30.27 (–CH_2), 27.38 (–CH_2), 26.05 (–CH_2), 25.85 (–CH_2), 25.73 (–CH_2); IR (KBr): ν cm^{-1}: 2927, 2886, 1765, 1696, 1340, 1026, 894, 745, 698.

*2.2.3. Poly-N-phenethylmaleimide (**7**)*

1.00 g (4.99 mmol) **1** was weighed into a glass vial and dissolved in 15 mL 1,2-dichlorobenzene. Air was displaced by argon and the vial was placed in a silicon bath at 150 °C. 16.4 mg (0.057 mmol) Luperox 130, dissolved in 0.2 mL 1,2-dichlorobenzene, was added. The reaction mixture was stirred at 150 °C for ~2 h. After cooling to room temperature, homopolymer **7** was precipitated by addition of petroleum ether, filtered off, washed with petroleum ether and dried in vacuum at 40 °C. **7** is soluble in acetone, THF, ethyl acetate, toluene, dioxane and chloroform, and insoluble in acetonitrile and methanol.

Yield: 861.4 mg off-white solid (86%), melting point: 436.7 °C; M_n (bimodal distribution) = 5600 and 17,600 g/mol; ^{1}H NMR ($CDCl_3$, δ, ppm): 7.70–6.65 (bs, 5H, H–Ar), 4.93–3.36 (bs, –*N*–CH_2– + –CH–), 3.16 (bs, –Ar–CH_2– + –CH–); ^{13}C NMR ($CDCl_3$, δ, ppm): 176.39 (C=O), 137.58 (C–Ar), 128.72 (C–Ar), 128.49 (C–Ar), 126.67 (C–Ar), 43.96 (–CH-succ), 40.55 (–*N*–CH_2–), 33.20 (Ar–CH_2–); IR (KBr): ν cm^{-1}: 3460, 3025, 2937, 1772, 1713, 1685, 1493, 1402, 1441, 1356, 1255, 1159, 1028, 746, 669.

2.2.4. Peroxide-initiated grafting

Grafting reactions were performed in 20 mL glass vials fitted with teflon septa and magnetic stirrer. In a typical experiment, 3.01 g (7.1 mmol) squalane was dissolved in 1,2-dichlorobenzene (10 mL). Air was displaced by argon and the vial was put in a 150 °C silicon oil bath. After 10 min 39.7 mg (0.14 mmol) Luperox, dissolved in 0.2 mL 1,2-dichlorobenzene, was added, followed by 140.3 mg (0.7 mmol) **1**, dissolved in 2 mL warm 1,2-dichlorobenzene. The reaction mixture was stirred at 150 °C for ~2 h. Two fractions of graft products were isolated. *Fraction 1* was obtained by filtration after addition of *n*-hexane (100 mL) to the reaction mixture. From the residual solution, the solvents as well as unreacted oligomer were distilled off under vacuum to give waxy *fraction 2*.

2.3. Analytical characterization of reference compounds and graft products

Melting points were determined with a Shimadzu DSC-50 differential scanning calorimeter (heating rate = 20 °C/min).

GC analysis was used to monitor the disappearance of the monomer, to verify complete consumption of **1** prior to fractionation and for a rough estimation of the amount of reacted squalane and eicosane. For the latter the solvent was used as internal standard. Analysis was carried out with a Perkin–Elmer 8500 gas chromatograph using a packed column OV-1.

Fourier transform infrared (FTIR) spectra were recorded on a Biorad FTS 135 with KBr pellets (*fraction 1*, reference substances, eicosane) and films between KBr plates (*fraction 2*, squalane), respectively.

^{1}H NMR spectra were recorded on a Bruker AC-E-200 FT NMR spectrometer operating at a proton frequency of 200 MHz. Deuterated chloroform ($CDCl_3$) and deuterated dimethyl sulfoxide (DMSO-d_6) were used as solvents and as reference. ^{1}H NMR spectroscopy was used to estimate the average number of grafts per substrate residue (n) by comparing the integrals of the phenyl protons in the 6.7–7.6 ppm region (I_{aryl}) and the remaining protons of the hydrocarbon substrate in the 0.6–1.8 ppm region (I_{ali}) (spectra in DMSO-d_6). For the calculation the following assumptions were made: either only single units are bonded to the backbone (n_1) or only one chain is grafted (n_2). Taking into account that grafting leads to a shift of substrate protons to >1.8 ppm, the average number of grafted residues can be calculated according to $n_1 = (H - 2)/(5 \times I_{\text{ali}}/I_{\text{aryl}})$ and $n_2 = H/(5 \times I_{\text{ali}}/I_{\text{aryl}} + 2)$, respectively, with H = number of protons of the substrate (squalane $H = 62$, eicosane $H = 42$). For squalane the calculation was also done assuming that grafting takes place only on tertiary atoms (n_1' and n_2').

^{13}C NMR spectra were recorded on a 200 MHz Bruker AC200 spectrometer and a 400 MHz Bruker Avance DRX400, respectively. Samples were dissolved in $CDCl_3$ and the solvent was used as reference. For graft products a modified recording technique was used: relaxation delay was prolonged from 1 s to 10 s and spectra were recorded with 15,000 scans instead of 2048.

UV spectra were recorded on a Hitachi U-2001 spectrometer. For low-molecular weight compounds acetonitrile was used as solvent. ($\lambda_{\max}$ of all succinimides = 252 nm, $\lambda_{\max}$ of **1** = 297 nm). Spectra of homopolymer were recorded in chloroform because of insolubility in acetonitrile.

The number and weight average molecular weights were determined by size exclusion chromatography (SEC) (Hewlett-Packard Chemstation 1100 system equipped with Styragel columns) at 40 °C with a flow rate of 1 mL/min. The solvent was THF and polystyrene standards were used for conventional external calibration. SEC analysis of *fraction 1* yielded the number of units per substrate molecule according to $n = (M_{\text{p}} - M_{\text{oligomer}})/M_{\text{monomer}}$, where M = molar mass and M_{p} = peak molecular weight.

MALDI-TOF MS, used for analysis of *fraction 1*, was performed on a Micromass TofSpec2E time-of-flight mass spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm, operated at 5 Hz) and a time-lag focusing unit. Ions were generated by irradiation just above the threshold laser power. The spectra were recorded in the reflectron mode with an acceleration voltage of 20 kV and externally calibrated with a suitable mixture of poly(ethylene glycol)s (PEG). Sample solutions were prepared by mixing a solution of dithranol in THF ($c = 10$ mg/mL), a solution of the analyte ($c = 5$ mg/mL), and a solution of CF_3COONa (NaTFA, $c = 1$ mg/ml), respectively, in a ratio of 7:2:2 (v/v/v). 0.5 μL of the mixture were deposited on the sample plate (stainless steel) and allowed to dry under air. The spectra of 150–200 shots were averaged to improve the signal-to-noise ratio. Polymer Processing 2.0 from Sierra Analytics was used for the calculation of number average molecular weight (M_{n}) and polydispersities from the MALDI-TOF mass spectra.

3. Results and discussion

N-phenethyl-maleimide (**1**) (Fig. 1) was chosen as model compound for aliphatic maleimides in order to increase the sensitivity of the analysis by selection of a monomer producing a graft which can readily observed by ^{1}H NMR spectroscopy. In addition, the phenyl group enables analysis by UV spectroscopy, which is a more sensitive method than NMR spectroscopy. **1** was prepared according to Reddy et al. [19] in a one-step procedure and purified by recrystallization from *n*-hexane. As reference substances for spectroscopical analysis, homopolymer and several succinimides were synthesized. *N*-phenethyl-succinimide (**2**) (Fig. 1) was obtained analogously to **1** in a one-step procedure [19] (yield 78%). *t*-Butyl-(**4**) and cyclohexyl-*N*-phenethyl-succinimide (**6**) were obtained by two-step procedures (Fig. 2) by reacting *t*-butylmercuric chloride (**3**) and cyclohexylmercuric chloride (**5**), respectively, which were synthesized according to the literature [20,21], with **1** analogous to Curran et al. [22] (overall yield **4**: 9%, **6**: 37%).

Synthesis of homopolymer **7** and the grafting reactions (molar ratios oligomeric substrate:**1**:peroxide = 10:1:0.2) were carried out at 150 °C under argon atmosphere in 1,2-dichlorobenzene as solvent. Luperox 130, the selected initiator, is well known to be particularly reactive in abstracting hydrogen atoms from C–H bonds of model hydrocarbon substrates and in polyolefin chains. The disappearance of the monomer from the reaction mixture was monitored by GC and it was found that after approx. 1 h complete conversion of the monomer was achieved. A rough estimation of the amount of reacted squalane and eicosane showed that only a very small percentage of the substrate was grafted (2–3%). Two fractions of graft products were isolated: *fraction 1* was obtained by precipitation with *n*-hexane, and waxy *fraction 2* was isolated from the residual solution after the solvents as well as unreacted oligomer had been distilled off under vacuum. The weight proportion of *fraction 1* was found to be 26% in eicosane and 23% in squalane experiments. Both fractions of graft products and all reference substances were analysed by FTIR, ^{1}H NMR, ^{13}C NMR and UV spectroscopy. *Fraction 1* was also analysed by SEC and MALDI-TOF MS.

Infrared spectroscopy is the most common analytical tool for grafted polyolefins, and it has been reported that FTIR can even be used to distinguish single MA grafts from oligomeric grafts and free homopolymer [23]. According to the authors, the band associated with the C=O of MA-PP can be resolved into two bands, which can be attributed to isolated succinic anhydride units and blocks of oligo(MA). Alkyl-substituted cyclic imides with a five-membered ring, as produced from maleimide grafting, should exhibit 2 bands in the range of 1680–1760 cm^{-1} corresponding to symmetric and asymmetric C=O stretching modes. All graft products and reference compounds exhibit absorptions in the expected range. A representative set of spectra for grafted hydrocarbon substrates and reference compounds is shown in Fig. 3 for both fractions of **1**-*g*-squalane, homopolymer **3** and succinimide **5**. A significant difference can be seen in the shape of the strong band due to symmetric stretching of C=O. *Fraction 1* isolated by filtration (a) and homopolymer **7** (c) show broad absorption bands that can be resolved into two bands centered at 1688 and 1706 cm^{-1} (a) and 1687 and 1710 cm^{-1} (c), respectively, whereas *fraction 2* isolated by distillation (b) and alkylsuccinimide **4** (d) show only one very sharp absorption band centered at 1701 and 1686 cm^{-1}, respectively. The broad signal in the spectrum of *fraction 1* suggests the presence of single units as well as oligomeric grafts and/or homopolymer, whereas *fraction 2* could contain mainly single units. Determination of the degree of functionalization from IR spectra was not possible due to the lack of a suitable reference band of the oligomeric substrate and an insufficient solubility of the reference succinimides in eicosane and squalane, not allowing the preparation of homogeneous mixtures needed for establishing a calibration curve.

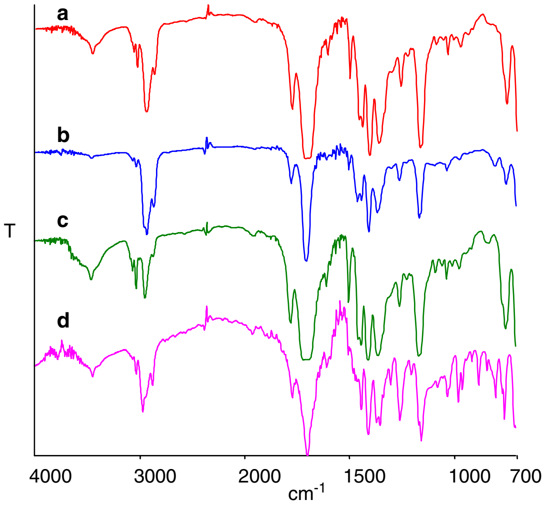

Fig. 3. IR spectra of **1**-*g*-squalane (a: *fraction 1*, b: *fraction 2*), **7** (c) and **4** (d).

Preliminary information regarding the nature of grafts can be obtained from ^{1}H NMR spectra. For eicosane as well as squalane spectra of both fractions were found to differ mainly in the relative intensities of characteristic resonances. Fig. 4 shows ^{1}H NMR spectra of *fraction 1* (a) and *fraction 2* (b) of **1**-*g*-eicosane and *fraction 1* (c) and *fraction 2* (d) of **1**-*g*-squalane. There are strong resonances in the region of the substrate protons and three strong resonances that are characteristic for **1**-derived material (aryl-H at 6.7–7.6 ppm, *N*–CH$_2$ at 3.4–3.9 ppm, CH$_2$-aryl at 2.6–3.1 ppm). Compared to the spectrum of the homopolymer (Fig. 5), in spectra of *fraction 1* the signals associated with the ethyl chain are somewhat better separated, whereas the corresponding peaks in *fraction 2* are well separated. The broad shoulder centered at 4.6 ppm characteristic for protons of succinimide moieties in long chains lacks in all graft products. Both reference succinimides (spectra not shown) show additional signals in the range of 2.4–2.6 ppm, which are associated with methylene protons in the succinimide rings, and peaks centered at 2.68 and 2.69 ppm, respectively, which are assigned to methine protons. These resonances are well separated from the aryl-CH$_2$ signals (triplet centered at 2.9 ppm). In spectra of *fraction 1*, resonances arising from ring protons apparently overlap with CH$_2$-protons of the ethyl chain and only a broad shoulder can be seen, which indicates the presence of oligomeric grafts. Intermediate protons of such grafts are known to be less observable than terminal protons because of a more broadening of the peak. In spectra of *fraction 2*, in the range of 2.3–2.8 ppm, several separate partially overlapping signals can be seen, which could be assigned to ring protons of single units.

The average number of grafts per eicosane and squalane molecule (n) was calculated from the relative intensities of resonances associated with the aromatic hydrogens of the 6.7–7.6 ppm region and the remaining protons of the substrate in the 0.6–1.8 region. For the calculation, spectra were recorded in DMSO-d_6 to avoid falsification of the results due to the CDCl$_3$ signal which overlaps with the resonances of the aromatic hydrogens. For both substrates two different values were determined: n_1 was calculated assuming that only single units are bonded to the backbone and n_2 on the assumption that each substrate molecule contains only one long-chain graft. In both cases it was considered that grafting on secondary carbons of the substrate molecule leads to

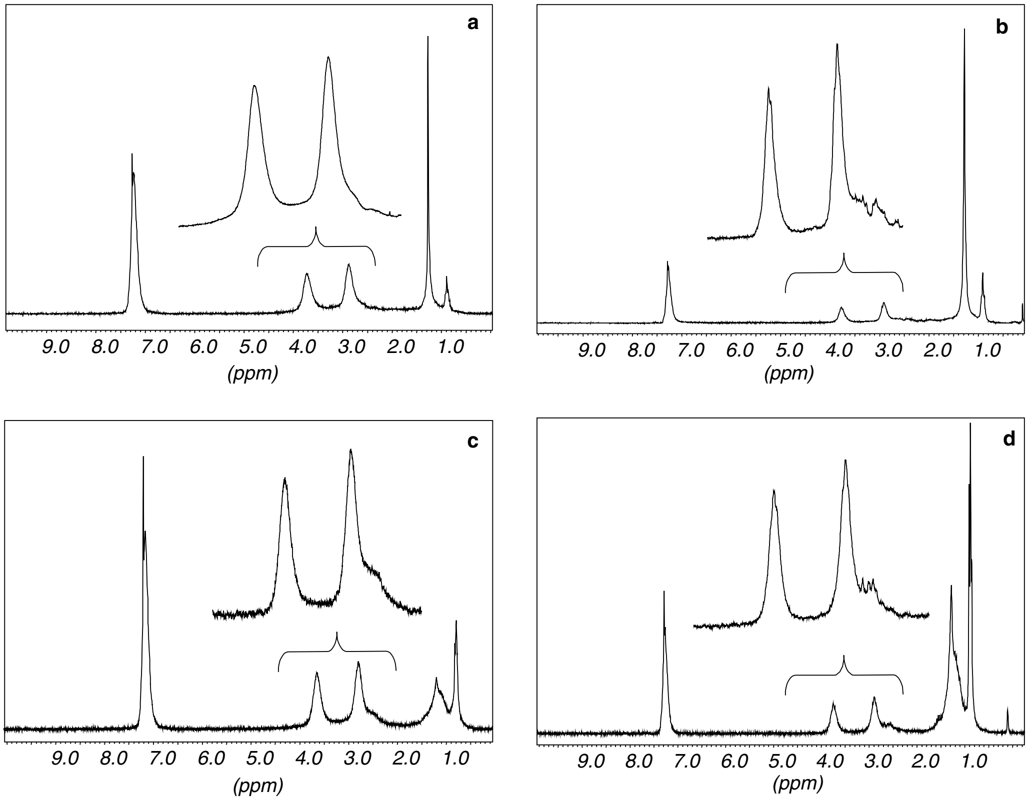

Fig. 4. ^{1}H NMR spectra ($CDCl_3$) of **1**-*g*-squalane (a: *fraction 1*, b: *fraction 2*) and **1**-*g*-eicosane (c: *fraction 1*, d: *fraction 2*).

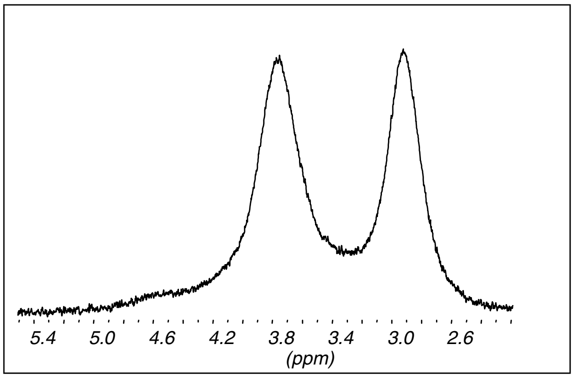

Fig. 5. Expanded view of the ^{1}H NMR spectrum of homopolymer **7**.

Table 1
Yields and average number of grafts per substrate residue (n)

Compound	Yield (wt%)	n_1[a] (n_1')[b]	n_2[c] (n_2')[b]	n_3[d]
1-*g*-Eicosane *fraction 1*	26	9.1	15.0	6.1
1-*g*-Eicosane *fraction 2*	74	2.8	3.1	–
1-*g*-Squalane *fraction 1*	23	9.4 (13.2)	13.7 (11.0)	5.3
1-*g*-Squalane *fraction 2*	77	2.6 (3.2)	3.3 (3.1)	–

[a] Determined by ^{1}H NMR spectroscopy assuming that only single units are grafted.

[b] Calculated assuming that grafting takes place only on tertiary carbons.

[c] Determined by ^{1}H NMR spectroscopy assuming that only one chain is grafted.

[d] Determined by SEC analysis.

a shift of the CH-proton at the grafting site to >1.8 ppm. For squalane the number of grafts was also calculated assuming that grafting takes place only on tertiary carbon atoms (n_1', n_2'). The results are summarized in Table 1. As an average number of units per substrate molecule very similar results were obtained for eicosane (*fraction 1* $n = 9.1$–15, *fraction 2* $n = 2.8$–3.1) and squalane (*fraction 1* $n = 9.4$–13.7, *fraction 2* $n = 2.6$–3.3). For *fraction 2* values were obtained which are comparable to results reported for grafting MA onto low molecular weight alkanes (typically 3–4 units), indicating intramolecular reactions. The very high number of grafts determined for *fraction 1* strongly indicates the presence of oligomeric grafts and/or low molecular weight homopolymers. For this fraction *n* was also roughly estimated by SEC analysis (n_3, Table 1), yielding 5.3 units per substrate molecule for squalane, and 6.1 units for eicosane. These values are significantly lower than results calculated from NMR spectra, which could be explained by the lack of appropriate standards, but also by the presence of homopolymer.

UV analysis was carried out to determine *n* by a highly sensitive method, uninfluenced by the grafting site on the substrate backbone, using a calibration curve established with reference compound **2**. All model succinimides showed absorption in the same range ($\lambda_{max} = 252$ nm). Surprisingly, negative values for *n* were obtained, revealing the presence of compounds with a very strong absorption in a range similar to that of alkyl succinimides. Comparing spectra of graft products and model succinimides (representative spectra shown in Fig. 6a–c), it can be seen that graft products and homopolymer absorb >280 nm. This could be explained by the presence of maleimide residues, which absorb strongly in this range ($\lambda_{max} = 297$ nm, spectrum d in Fig. 6). As will be discussed later in detail, the results of analysis by MALDI-TOF MS suggest that such groups are contained in *fraction 1*. UV spectroscopy, which is a highly sensitive analytical method, indicates the presence of maleimide groups formed by termination via disproportionation or loss of a hydrogen atom from a single succinimide radical, similar to the findings of Ranganathan et al. [8] for MA-grafting in both fractions of graft products. The proportion of unsaturated groups seems to be too small to be detected by ^{1}H NMR spectroscopy, since no resonances of C=CH protons can be observed in the expected range (somewhat high-field shifted compared to the maleimide-H resonances of **1** at 6.7 ppm).

^{13}C NMR spectroscopy was employed to elucidate the structure of the grafts and to determine the position of the grafts at the substrate backbone in products obtained by grafting of squalane. In order to facilitate the assignment of the resonances, DEPT NMR spectra were also recorded (spectra except for one not shown).

Expanded views of ^{13}C NMR spectra of *fraction 1* and *fraction 2* of **1**-*g*-eicosane are provided in Fig. 7a and b, respectively. In both spectra all typical substrate signals are present, and the chemical shifts match that of pure substrate. All resonances are only slightly low-shifted (0.1–0.15 ppm). In both spectra there are strong resonances at 39.8 ppm and 33.4 ppm arising from the CH_2-groups of the ethyl chain, but apart from this the spectra show significant differences, clearly indicating different types of grafts. The spectrum of *fraction 1* contains a very broad signal centered at 176.5 which can be assigned to the carbonyl groups of the succinimide ring, and a weak and also very broad signal in the range of 41–45 ppm, which is most probably due to the ring CH carbons. Both resonances match that of homopolymer **7** (Fig. 8) with respect to the chemical shifts and to the width of the signals. In the region where the methylenes of the ring would be expected (30–32 ppm according to reference compounds **4** and **6**) only a weak resonance can be observed. These results strongly

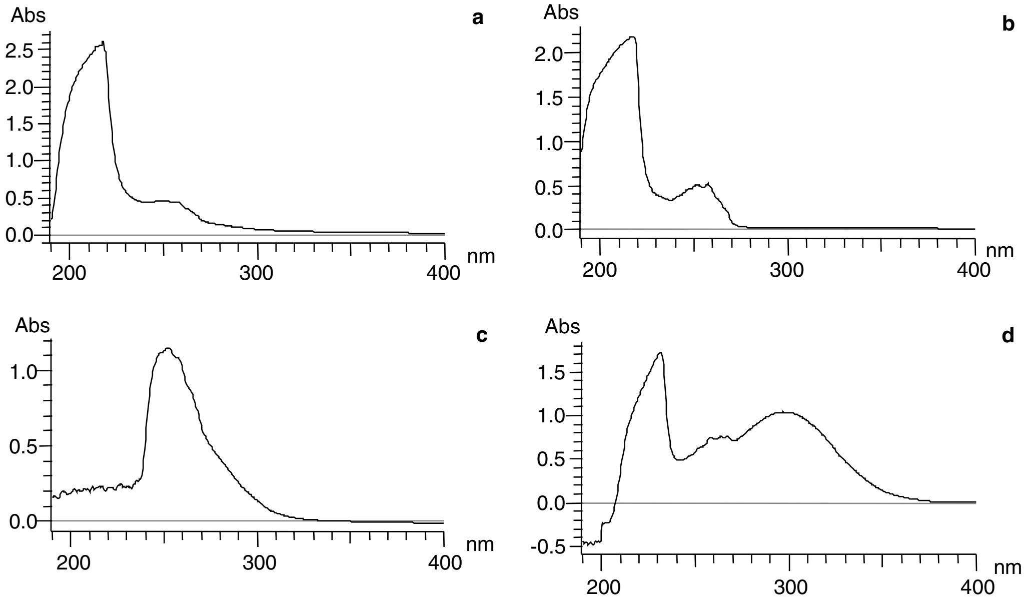

Fig. 6. UV-spectra of **1**-*g*-squalane (a), **4** (b), **1** (c) and **7** (d).

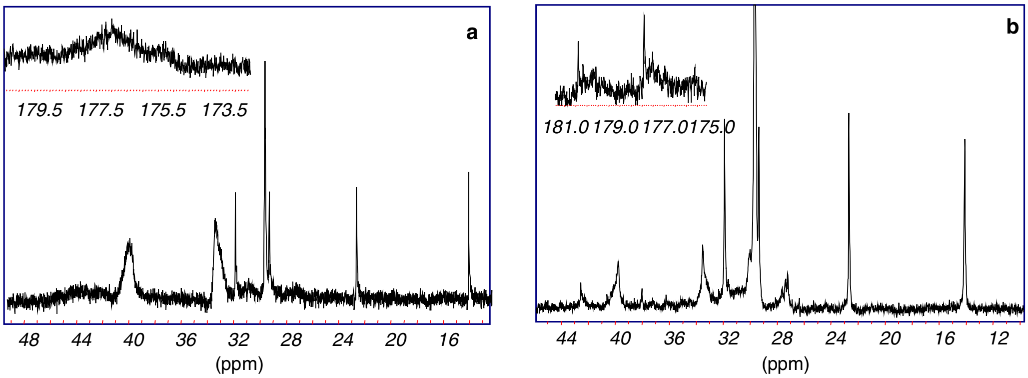

Fig. 7. ^{13}C NMR spectra of *fraction 1* (a) and *fraction 2* (b) of **1**-*g*-eicosane.

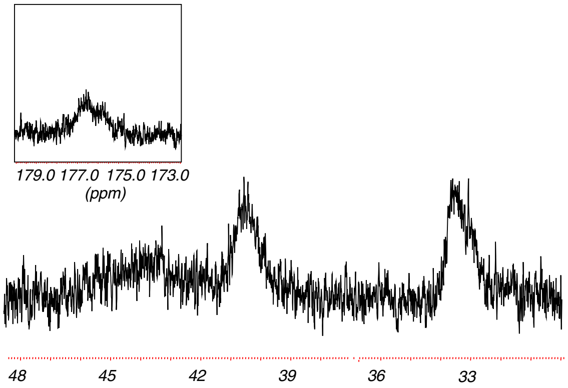

Fig. 8. Expanded view of the ^{13}C NMR spectrum of homopolymer **7**.

suggest the presence of oligomeric grafts, since such a high number of grafts contained in *fraction 1*, according to ^{1}H NMR analysis, should result in stronger and less broadened signals if linked to the substrate as single units. This assumption is also supported by the absence of resonances which can be assigned to CH–carbons of grafting sites and to the fact that apart from a weak and broad resonance at 27.4 ppm, which according to DEPT NMR spectra arises from methylene groups, no substrate signals shifted due to the proximity to grafting sites can be observed. In the spectrum of *fraction 2* there is also a methylene resonance centered at 27 ppm, but contrary to the *fraction 1* spectrum this signal is very strong. There are some weak resonances in the range of 36–38 ppm, which could be assigned to CH–carbons of grafting sites. The chemical shifts of the strong signals at 179 and 176 ppm agree very well with those of the carbonyl resonances of the alkyl succinimides **4** and **6**. The chemical shift of the resonance at 42.6 ppm is in the expected range of that of a methine group of the succinimide ring attached to a secondary carbon atom. The corresponding resonance in reference compound **6** is at 45 ppm, but a high-field shift can be expected by bonding to a linear hydrocarbon residue. The strong signal at 30 ppm (partially overlapping with methylene resonances of the substrate, but nevertheless clearly visible) can be assigned to methylenes of the succinimide ring. These results provide strong evidence for grafts consisting mainly of single units, although the presence of some oligomeric units cannot be excluded. Taking into account that *fraction 2* contains the major proportion of graft products (74 wt%) and that according to ^{1}H NMR analysis multiple grafts are present, it can be assumed that propagation by intramolecular hydrogen transfer plays an important role in the chain process.

Expanded views of ^{13}C NMR spectra of *fraction 1* and *fraction 2* of **1**-*g*-squalane are provided in Fig. 9a and b, respectively. Again, in both fractions all typical substrate signals are found at chemical shifts, which apart from a slight low-shift match that of pure substrate. Strong evidence for the presence of mainly oligomeric grafts in *fraction 1* is provided by the broad resonances centered at 176 ppm (C═O) and 43.8 ppm (ring methine). The chemical shifts match that of homopolymer and *fraction 1* of **1**-*g*-eicosane. The methylene resonances at 31 ppm could arise from substrate carbons adjacent to grafting sites. No resonances >46 ppm matching that of methines grafted to tertiary carbons (found at 49.4 ppm in spectra of **4**) and no quaternary carbons are observed, indicating that grafting takes place mainly on secondary carbon atoms of the substrate. As for the eicosane experiments, mainly graft products with single units seem to be contained in *fraction 2*. This is indicated by the strong carbonyl signals at 174–179 ppm as well as the resonances at 48.3 and 46.9 ppm, which can be assigned to methine groups of the succinimide ring attached to different tertiary carbons of the substrate. The corresponding resonances of quaternary carbons of squalane are at 38.2 and 35.6 ppm. As can be clearly seen in the DEPT

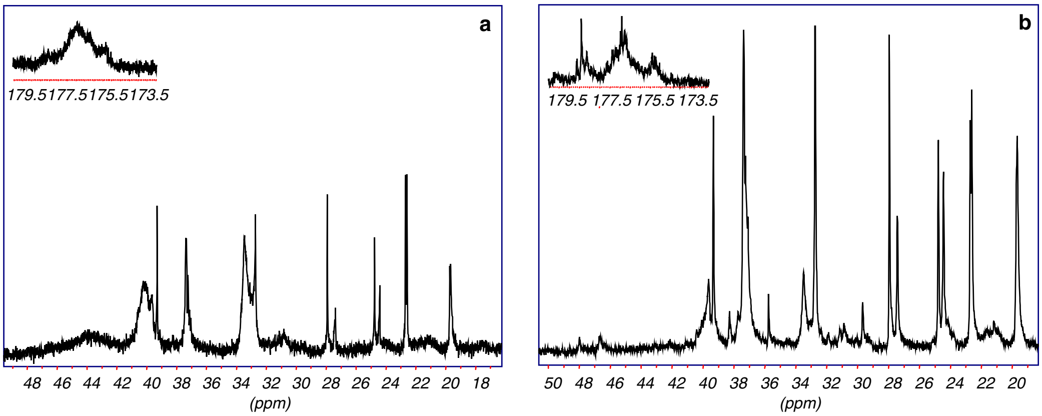

Fig. 9. ^{13}C NMR spectra of *fraction 1* (a) and *fraction 2* (b) of **1**-*g*-squalane.

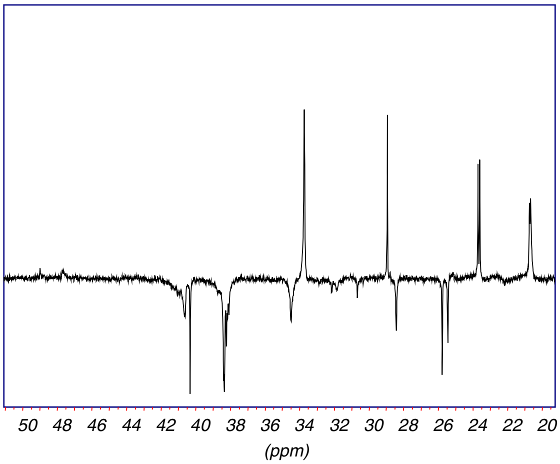

Fig. 10. DEPT NMR spectrum of *fraction 2* of **1**-*g*-squalane.

NMR spectrum of *fraction 2* (Fig. 10, positive signals for CH/CH_3 and negative for CH_2), these surprisingly strong signals disappear on going from the normal mode to the DEPT mode. The CH_2-resonances at 31 ppm are most probably due to substrate methylenes adjacent to grafting sites. The signal at 30 ppm can be assigned to methylenes of the succinimide ring, matching the chemical shift of the corresponding resonances in *fraction 2* of **1**-*g*-eicosane. According to the literature, grafting should take place mainly at tertiary carbons. The findings that for *fraction 2*, which contains the most graft products (77 wt%), the single units are mainly located on tertiary sites of a squalane molecule—although long-chain grafts mainly located on secondary carbons are also formed under the chosen reaction conditions—indicate that propagation by homopolymerization is sterically hindered. Taking into account that multiple grafts are formed, it can be assumed that propagation occurs to a large extent by intramolecular hydrogen abstraction. The lack of grafts at secondary carbons, as expected if intramolecular propagation proceeds by way of a six-membered ring, indicates that either the resulting secondary radicals are transformed into a more stable tertiary radical, or that terminative hydrogen transfer does not involve a six-membered transition state as suggested by Heinen et al. [5].

To further elucidate the structure of the graft products in *fraction 1* and to determine if homopolymer was formed, MALDI-TOF MS was employed. A series of preliminary experiments was necessary to find out that dithranol is a suitable matrix for the investigation of these products. Apart from signals which could be assigned to pseudo-molecular ions $[M \cdot H]^+$ of oligomers $R'–(\mathbf{1})_n–R''$ with different end groups R' and R'', respectively (compare discussion below), $[M \cdot Na]^+$ ions were observed due to traces of sodium. It was found that the intensities observed for $[M \cdot H]^+$ ions relative to corresponding $[M \cdot Na]^+$ ions were rather difficult to reproduce, even when spectra were acquired from the same spot. For several samples the $[M \cdot Na]^+$ signals even dominated the MALDI spectra. Thus, NaTFA was generally added during the sample preparation for MALDI. Under these conditions reproducible spectra could be obtained and the comparability of the spectra of different samples be improved. Due to the increased sodium concentration all spectra were dominated by pseudo-molecular ions $[M \cdot Na]^+$. As an example, the MALDI spectrum of **1**-*g*-squalane (Fig. 11), and an expanded view of the mass range 1150–1700 Da (Fig. 12) are provided. The most important series of the spectrum is interpreted as $Sq–(MI')_n–H$ (see Fig. 13 for definition of units) ionized by attachment of Na^+ (e.g. degree of polymerization $n = 5$: $[C_{90}H_{117}N_5O_{10} \cdot Na]^+$, $m/z_{obs} = 1450.86$, $m/z_{calc} = 1450.87$ Da; $n = 6$: $[C_{102}H_{128}N_6O_{12} \cdot Na]^+$, $m/z_{obs} = 1651.92$, $m/z_{calc} = 1651.95$ Da). The signal at

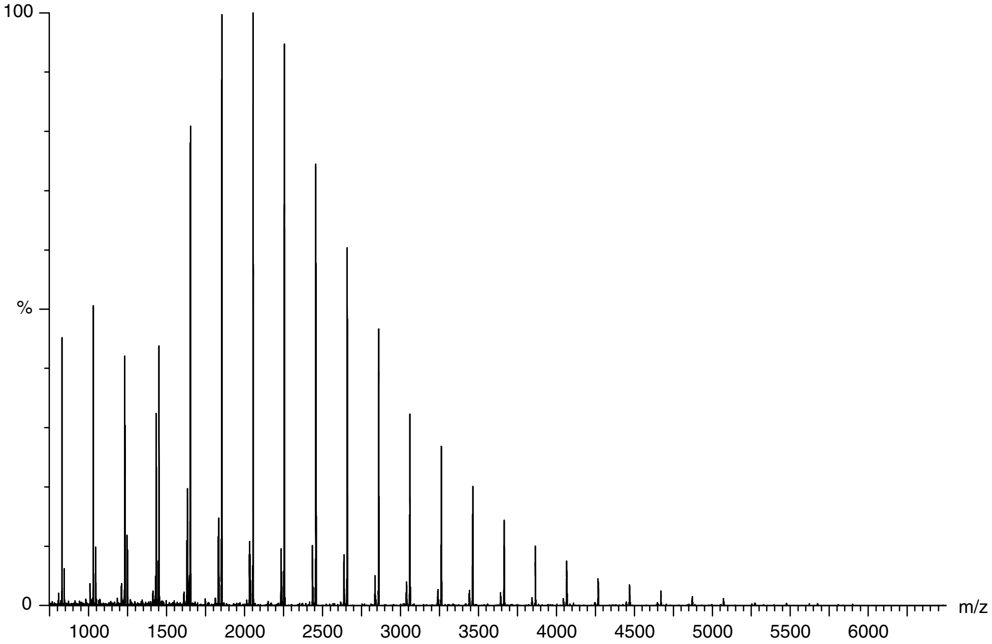

Fig. 11. MALDI-TOF mass spectrum of *fraction 1* of **1**-*g*-squalane.

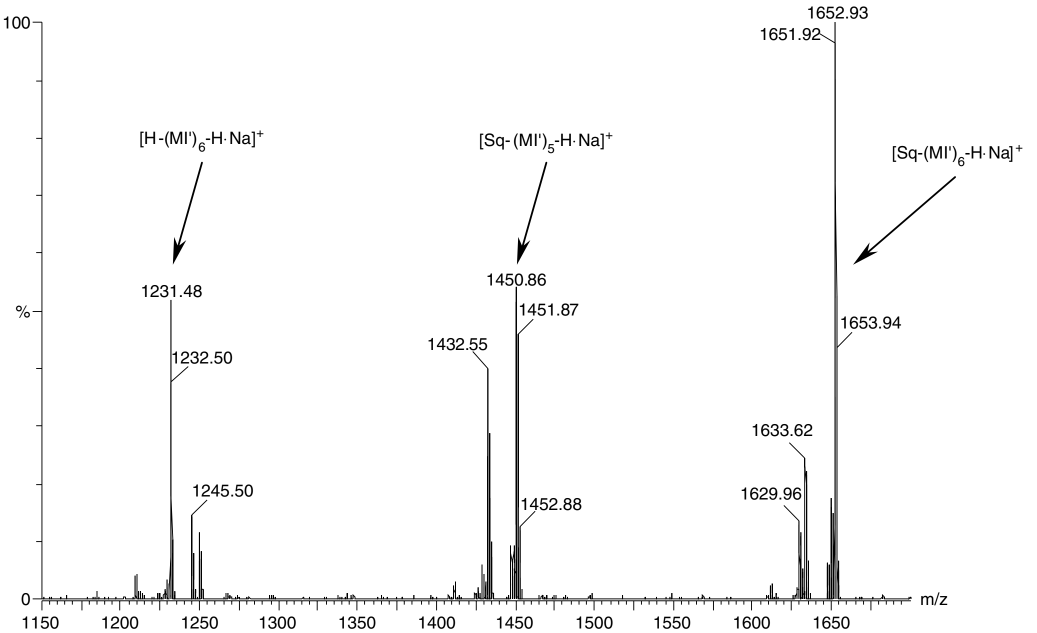

Fig. 12. Expanded view of the mass range 1150–1700 Da of the MALDI-TOF mass spectrum of **1**-*g*-squalane (*fraction 1*).

$m/z_{\mathrm{obs}} = 1629.96$ Da is assigned to the monoisotopic peak of a corresponding protonated species $[\mathrm{Sq{-}(MI')_6{-}H \cdot H}]^+$ ($[\mathrm{C_{102}H_{128}N_6O_{12} \cdot H}]^+$, $m/z_{\mathrm{calc}} = 1629.97$ Da). For both substrates graft products with $n = 4$–12 were observed. The maximal intensity of $[\mathrm{R{-}(MI')_n{-}H \cdot Na}]^+$ was found at $n = 7$. The important series of ions in the lower mass range of the spectrum is interpreted as $[\mathrm{H{-}(MI')_n{-}H \cdot Na}]^+$ (e.g. $n = 6$:

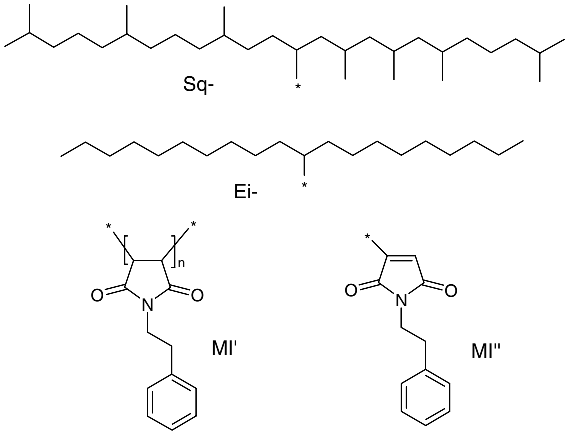

Fig. 13. Definition of units (note that Sq- and Ei- show only one possible isomer).

$[C_{72}H_{68}N_6O_{12} \cdot Na]^+$, $m/z_{obs} = 1231.48$ Da, $m/z_{calc} = 1231.48$ Da), indicating chain transfer to the monomer. Such transfer reaction are usually neglectable under typical grafting conditions. Apparently, at the relatively high concentration used in our studies (0.1 M) chain transfer to monomer is a factor. It has to be mentioned that squalanes substituted with more than one $–(MI')_n–H$ side chain could have equal masses, e.g. a doubly substituted product $H–(MI')_2–Sq'–(MI')_8–H$ would have the same mass as $Sq–(MI')_{10}–H$. The findings that the average degree of polymerization of the series $Sq–(MI')_n–H$ is only slightly above the value observed for the series $H–(MI')_n–H$ ($n = 4–10$, maximal intensity at $n = 6$) indicate that double or higher substitution does not play an important role, in agreement with the results obtained by ^{13}C NMR spectroscopy. The fact that only products with $n \geqslant 4$ are observed indicates that homopolymers with $n \leqslant 3$ could be contained in *fraction 2*.

These two types of products were generally observed with the highest intensities in the MALDI-TOF mass spectra of Sq- as well as Ei-samples. But other series, which were generally observed with lower intensities, have to be mentioned too. First of all, a series of species with monoisotopic peaks 2 Da below the series $Sq–(MI')_n–H$ and $Ei–(MI')_n–H$ was found. This series can be interpreted with products like $Sq–(MI')_{n-1}–MI''$ and $Ei–(MI')_{n-1}–MI''$ as well as products with one double bond in the substrate chain. As an example, the signal at $m/z_{obs} = 1649.94$ Da (Fig. 14) can be interpreted as the monoisotopic peak of $[Sq–(MI')_5\text{-}MI'' \cdot Na]^+$ and $[Sq = (MI')_6 \cdot Na]^+$, respectively ($[C_{102}H_{126}N_6O_{12} \cdot Na]^+$, $m/z_{calc} = 1649.93$ Da). Taking into account that double bonds located within the backbone of the substrate could not cause the strong absorption observed in UV spectra, one can assume that this series of signals is mainly due to maleimide residues formed by disproportionation. Signals assignable to products with an additional double bond equivalent were also found in the vicinity of the species $H–(MI')_n–H$ (Fig. 15), which supports this assumption. In spectra of squalane signals with lower intensity 1 and 2 Da below the series of species interpreted as $Sq–(MI')_{n-1}–MI''$ can also be observed (see Fig. 14, additional signals 1 and 2 Da below 1649.94 Da). Note that such additional signals are not found in spectra of **1**-*g*-eicosane (Fig. 16). These signals could indicate that the reactions leading to one additional double bond equivalent in the products might occur a second time. The presence of two maleimide-terminated grafts on the same substrate molecule seems highly implausible. Somewhat more likely is that these signals are due to graft products with one maleimide group and a double bond arising from radicals formed at tertiary carbons of the substrate. It should be noted that no graft products due to β-scission of squalane were observed.

Furthermore, in all spectra a series was observed 14 Da above the signals assigned to $H—(MI')_n–H$, having an intensity comparable to the signals due to maleimide-terminated homopolymers. This series could be interpreted as $H–(MI')_n–CH_3$ (Fig. 15; $n = 6$: $[C_{73}H_{70}\text{-}N_6O_{12} \cdot Na]^+$, $m/z_{obs} = 1245.50$, $m/z_{calc} = 1245.49$ Da). Analogous $–CH_3$ terminated products $Sq–(MI')_n–CH_3$ (Fig. 14) and $Ei–(MI')_n–CH_3$, (Fig. 16) were not detected, clearly indicating initiation of homopolymerization by methyl radicals. Such radicals arise from the decomposition of Luperox 130. If not trapped with substrate, the initially formed *t*-butyloxy radicals undergo β-scission to give methyl radicals, which are known to initiate homopolymerization rather than abstracting hydrogen.

From the relative intensities of the signals in the spectra the proportion of the different products contained in *fraction 1* was calculated. A correct calculation for each individual species was impossible due to the presence of ions $[M \cdot H]^+$ in most samples (compare Figs. 14 and 16) with a relative intensity of approx. 10–40% in comparison to the corresponding ions $[M \cdot Na]^+$ and the series of ions of species with interfering isotope pattern, e.g. $[Sq–(MI')_n–H \cdot Na]^+$ and $[Sq–(MI')_n–MI'' \cdot Na]^+$. But three groups of products could be well separated: one group corresponding to the sum of all products that contain one squalyl or eicosyl group, one group corresponding to homopolymer, and one group containing H_3C-terminated homopolymer. It was found that *fraction 1* of the squalane experiments consists of 74% graft products, 17% homopolymer and 9% methyl-terminated homopolymer and *fraction 1* of the eicosane experiments of 82% graft products, 12% homopolymer and 6% methyl-terminated homopolymer. Taking into account the gravimetrically determined yields for *fraction 1*, it can be estimated that a total of only approximately 6 and 9%, respectively of the initially added amount of monomer

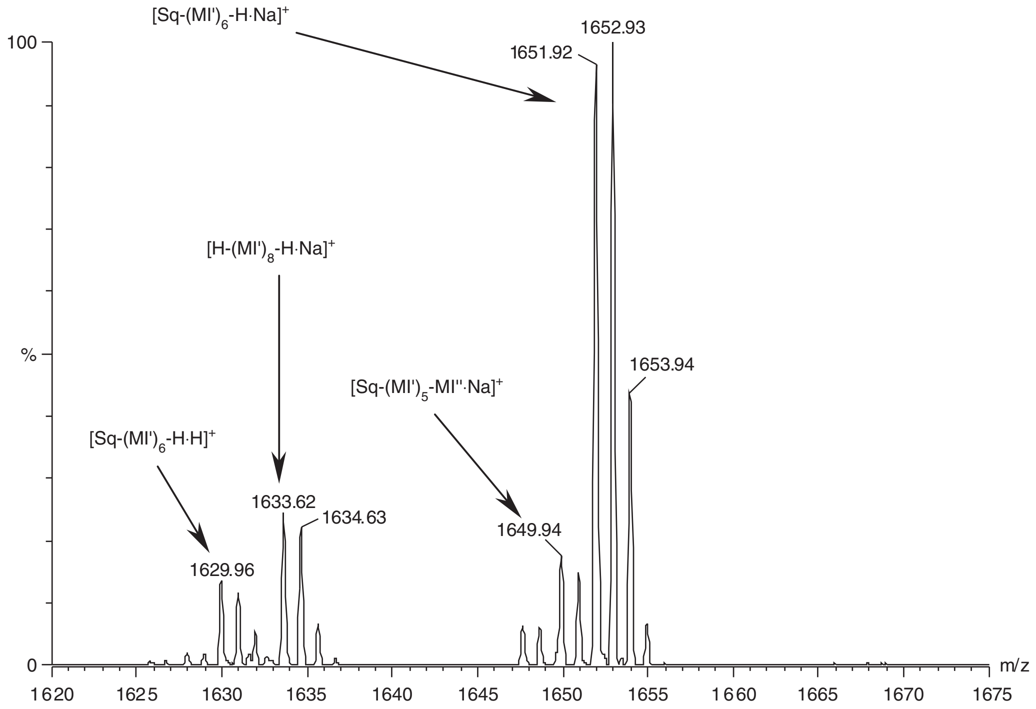

Fig. 14. Expanded view of the mass range 1620–1675 Da of the MALDI-TOF mass spectrum of **1**-*g*-squalane (*fraction 1*).

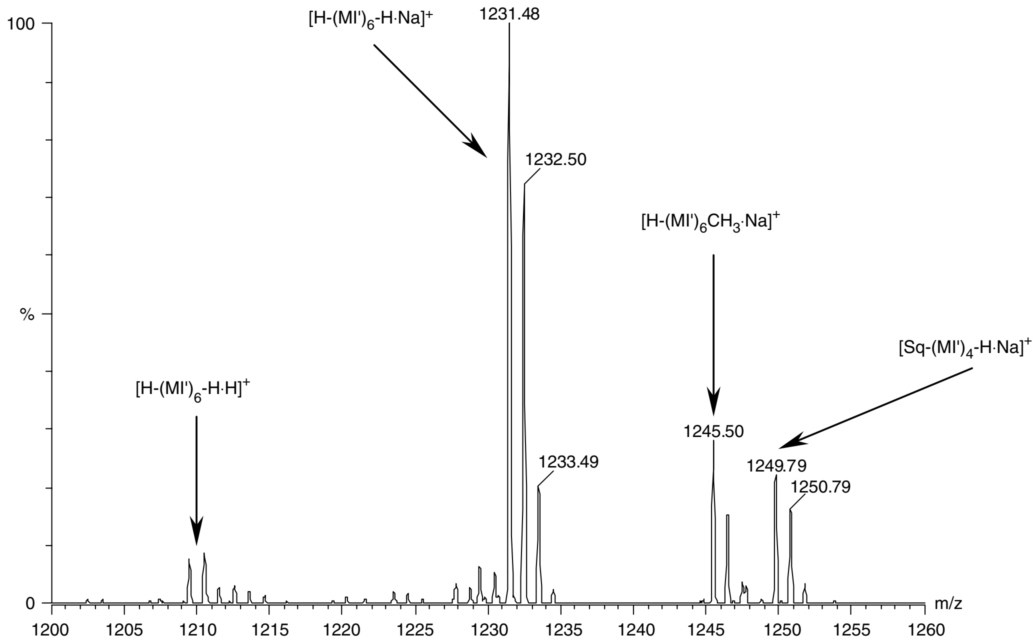

Fig. 15. Expanded view of the mass range 1200–1260 Da of the MALDI-TOF mass spectrum of **1**-*g*-squalane (*fraction 1*).

is not grafted to the substrate. The somewhat higher amounts of homopolymer obtained by grafting of squalane could be attributed to a higher sterical hindrance of the grafting reaction.

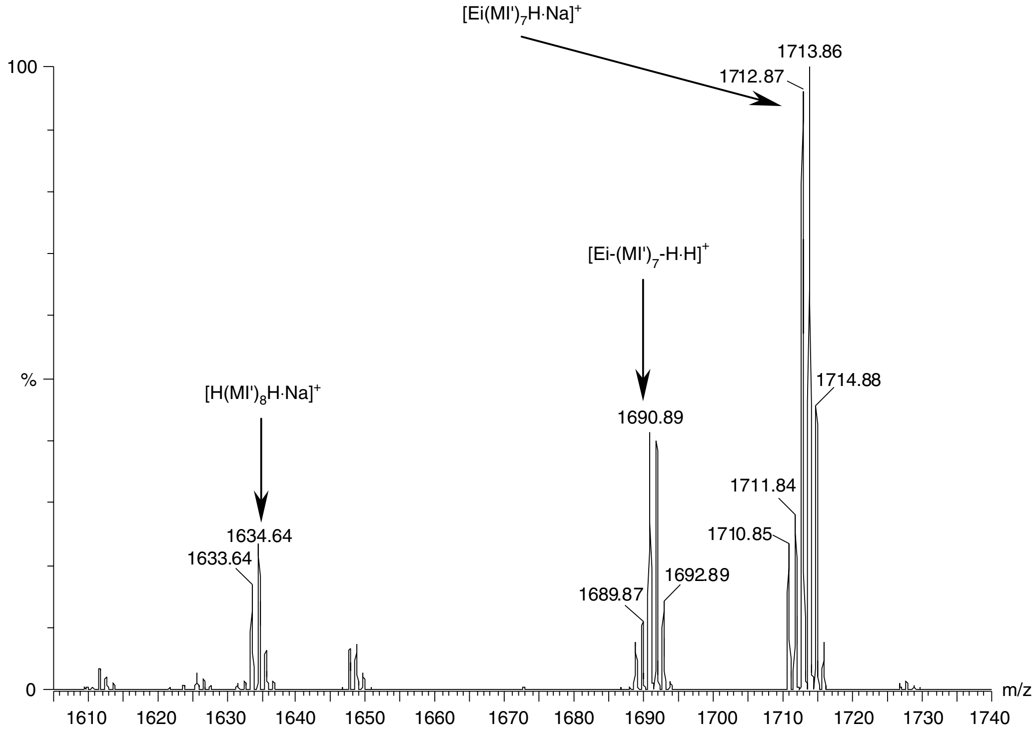

Fig. 16. Expanded view of the mass range 1605–1740 DA of the MALDI-TOF mass spectrum of **1**-*g*-eicosane (*fraction 1*).

4. Conclusion

Grafting of **1** as a model compound for aliphatic maleimides to eicosane and squalane yielded overall grafting yields of >90%, cleary showing the low tendency to homopolymerize under grafting conditions. Two fraction of graft products were isolated, which according to FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy differ distinctively with respect to the microstructure of the grafts. According to ^{1}H NMR analysis the major part of the graft products (~75 wt%) contains approx. 3 units per substrate molecule and ^{13}C NMR analysis provides strong evidence for a high proportion of grafts consisting of single succinimide units. Based on these results it can be concluded that propagation steps in maleimide grafting can be assumed to be similar to those for MA grafting, i.e. addition of monomer to a hydrocarbon radical followed by inter- or intramolecular hydrogen abstraction. Analysis of the minor fraction of graft products showed that the competing process of addition of monomer to give longer grafts plays a more important role than in MA grafting. According to MALDI-TOF MS, which was for the first time used for the analysis of products obtained by grafting of model hydrocarbons, oligomeric grafts with an average chain length of approx. 7 units are formed. This finding is substantiated by other spectroscopic observations. MALDI-TOF MS also revealed the presence of homopolymers with similar chain length, indicating that in the case of long-chain grafts double or higher substitution does not play an important role. Homopolymerization seems to occur partly by radical transfer to the monomer and partly by secondary radicals arising from decomposition of the peroxide (ratio approx. 2:1). The fact that mainly saturated products are found indicates that termination proceeds mainly by hydrogen transfer. The presence of some maleimide residues in the fraction of products containing homopolymer and long-chain graft products can be explained by termination via disproportionation. The level of maleimide units is too low to be detected by ^{1}H and ^{13}C NMR spectroscopy. According to UV analysis such groups are also present in the major fraction of products. Experiments to find a suitable matrix for analysis of this fraction by MALDI-TOF MS are in progress. ^{13}C NMR analysis gives strong evidence that in squalane long-chain grafts are located mainly on secondary carbons of the substrate, whereas single units are attached predominantly to tertiary sites. These results indicate that propagation by addition of a monomer to a succinimide radical grafted to tertiary carbons is sterically hindered. The lack of single grafts at secondary carbons, expected if intramolecular propagation proceeds by way of a six-membered ring, indicates that either the resulting secondary radicals are readily transformed into a more stable tertiary radical, or that terminative hydrogen transfer does not involve a six-membered transition state.

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