Grafting of Functional Maleimides onto Oligo- and Polyolefins

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Summary: In this paper the modification of polyolefins, especially polypropylene (PP), with maleimides is discussed. As there are many problems associated with the analysis of the grafting reaction, commercially available squalane and eicosane were used as model compounds for ethylene-propylene-copolymer (EPR) and polyethylene (PE). 2,4,6,8-Tetramethylnonane (TMN) was synthesized as a novel model compound for PP.
N-Phenylmaleimide and maleimido benzoic acid were grafted onto the oligomers in solution using 2,5-dimethyl-2,5-di-(tert-butyl-peroxy)-3-hexyne (Luperox 130) as radical initiator. The grafting efficiency was determined by NMR-, UV-spectroscopy, gravimetry and gas-chromatography. The influence of several reaction parameters on homopolymerformation, amount of modified oligomer and grafting efficiency could be elaborated. NMR-spectroscopy and SEC were used to analyse the nature of the grafts. Grafting yields were almost quantitative using up to more than 10 mol% monomer, but dropped at higher monomer concentrations to about 60%. The amount of modified oligomer could be increased with higher monomer concentrations or reaction temperatures.
Grafting of polymers was done by reactive extrusion. Products were analysed by IR-spectroscopy. Optimal grafting yields could be achieved with 1 wt% monomer and 0.5 wt% peroxide concentration.

Introduction

Modification of polyolefins to improve their processing characteristics and end-use properties has attracted considerable interest in recent years [1]. Due to the lack of functional groups applications of polyolefins are limited when adhesion, dyeability or compatibility with other polymers is needed. The most important procedures of functionalization comprise graft reactions of polyolefins with reactive monomers i.e. maleic acid anhydride and maleic acid esters [2-4]. Such modifications yield single monomer grafts or short length grafts changing substantially the polymer's reactivity and chemical and mechanical properties.

Concerning this our interest has been directed to study the grafting reactions of maleimides which have been scarcely considered in the literature up to now [5-7].

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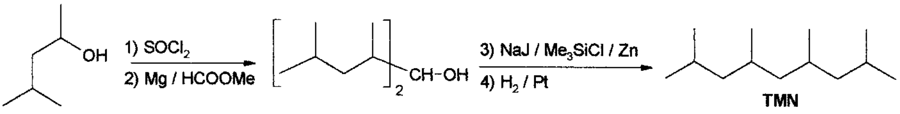
The present work is concerned with the modification of polyolefins with maleimides. As there are many problems associated with the analysis of the grafting reaction, commercially available squalane and eicosane were used as model compounds for EPR and PE. Additionally 2,4,6,8-tetramethylnonane (TMN) was prepared as novel model compound for PP.

Synthesis of 2,4,6,8-tetramethylnonane (TMN) and functional maleimides

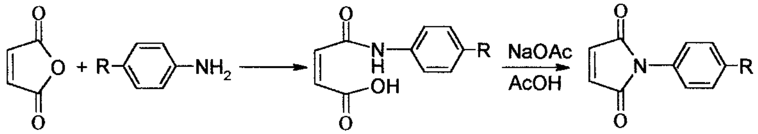
TMN was synthesized in a four step procedure using convenient organic methods starting from 4-Methylpentane-2-ol (Scheme 1) with an overall yield of 55%.

2-Chloro-4-methylpentane was obtained from the corresponding alcohol by treatment with thionyl chloride. 2,4,6,8-Tetramethylnonan-5-ol was synthesized by subsequent Grignard type reaction with formic acid methylester. The alcohol was reduced to the target compound TMN using the method of Morita et al. [8]. Due to the tertiary cabon atoms in α-position to the OH-functionality alkene formation up to 40% was observed and thus catalytic hydrogenation was necessary. TMN was distilled twice prior to use.



Scheme 1: Synthesis of TMN

N-Phenylmaleimide (**1**) and maleimidobenzoic acid (**2**) were obtained by reaction of aniline and 4-aminobenzoic acid with maleic acid anhydride and subsequent cyclization in a mixture of acetic acid and sodium acetate (Scheme 2).



1: R = -H
2: R = -COOH

Scheme 2: Synthesis of maleimides

Modification of oligomers

In a first series grafting reactions with **1** were generally carried out at 150°C under nitrogen atmosphere in 1,2-dichlorobenzene as solvent with molar ratios oligomer:monomer:initiator = 10:1:0.2. Since homopolymer of **1** (PPM) is insoluble in 1,2-dichlorobenzene, homopolymerisation during the grafting reactions was indicated by precipitation of PPM or by cloudy reaction mixtures.

Grafting of **1** onto squalane with di-t-butylperoxide, azobisisobutyronitrile and 1,5-dimethyl-1,5-di-(tert-butylperoxy)-hex-3-ine (Luperox 130; Elf Atochem) as initiators yielded graft-products without formation of PPM. With Luperox 130 the highest amounts of grafted oligomer were found. With dicumylperoxide mainly PPM was obtained. Surprisingly dibenzoylperoxide yielded neither homopolymer nor grafted oligomer. For comparison maleic anhydride (MA) was grafted onto squalane with dibenzoylperoxide as initiator. Using the same reaction conditions, MA-g-squalane could be synthesized, but for polymerisation of N-phenylmaleimide (**1**) this peroxide seems to be unsuitable, an effect which was not further investigated.

From the first series with **1** and Luperox 130 two fractions of graft-products were isolated. *Fraction 1* was obtained by filtration after addition of n-hexane to the reaction mixture. From the residual solution the solvents as well as unreacted oligomer were evaporated in vacuo to give *fraction 2*. The amount of unreacted oligomer was determined by GC analysis before precipiation and it was shown that only 1.1 wt% of squalane, 1.5 wt% of eicosane and 3.3 wt% of TMN were grafted.

The number of N-phenyl succinimide units / oligomer was determined by NMR spectroscopy.

According to literature [8, 9] ^{1}H-NMR spectra of maleic acid anhydride grafted onto squalane show signals at about 3.0 ppm which can be assigned to single units, short side chains appear at 4.2 ppm. The ^{1}H-NMR spectrum of homopolymer of N-phenylmaleimide (PPM) (Figure 1) shows signals at approx. 4.3 ppm, corresponding to the hydrogen atoms of the polymer backbone and from literature it is well known, that N-phenylsuccinimide gives signals at approx. 2.8 ppm.

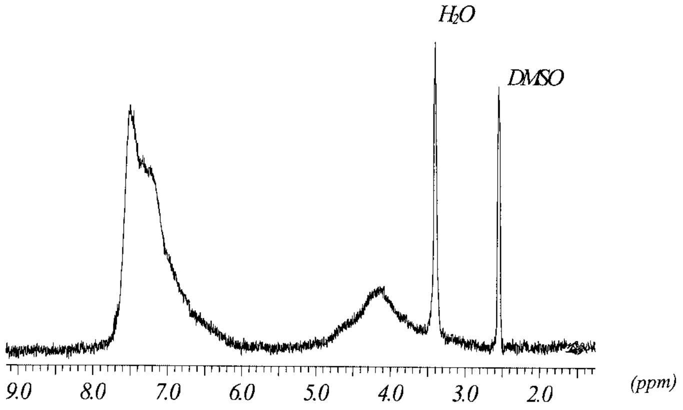


Fig. 1: ^{1}H-NMR spectrum of N-phenylmaleimide homopolymer (PPM)

The ^{1}H-NMR spectra of *fraction 1* of **1**-g-squalane (Fig. 2) and **2**-g-squalane (Fig. 3) show signals at 3.0 ppm and 4.2 ppm, indicating that single units as well as short side chains are formed by grafting of maleimides onto the oligomers.

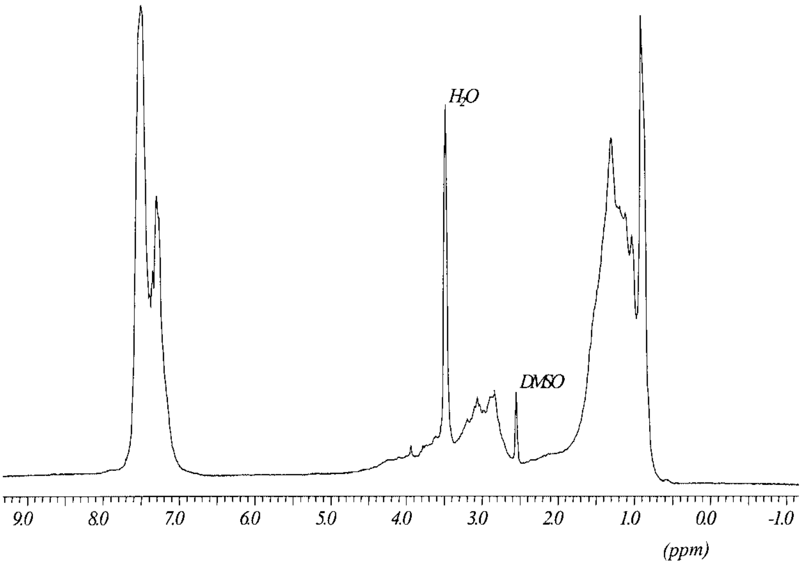


Fig. 2: ^{1}H-NMR spectrum of **1**-g-squalane (*fraction 1*)

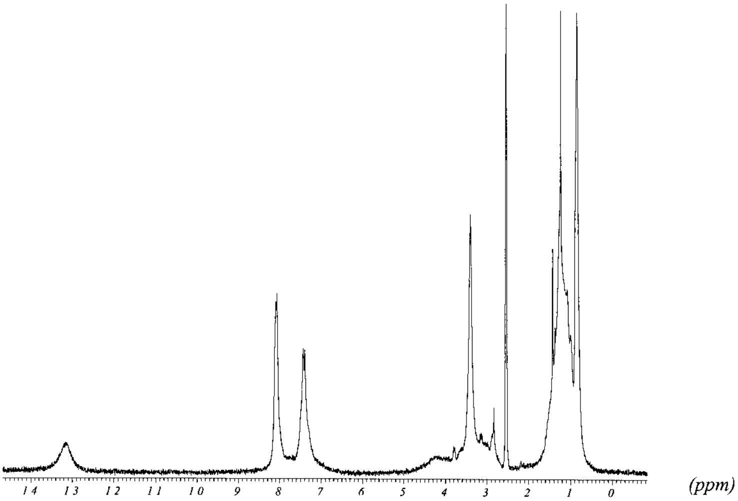


Fig. 3: ^{1}H-NMR spectrum of **2**-g-squalane (*fraction 1*)

Since hydrogen atoms at tertiary carbons appear in squalane as a broad multiplett at 1.5-1.7 ppm (Fig. 4) and in **1**-g-squalane and **2**-g-squalane (Fig. 2 and 3) no such peaks can be seen, it can be concluded that maleimides are preferrably grafted onto the tertiary carbons of the model compounds due to the higher reactivity of tertiary hydrogen atoms in hydrogen abstraction processes.

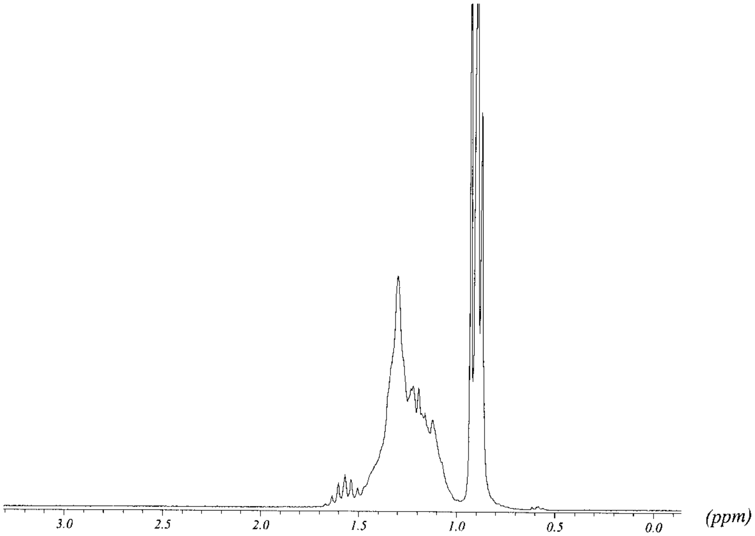


Fig. 4: ^{1}H-NMR spectrum of squalane

The grafting yields determined gravimetrically (*fraction 1 + 2*), the ratios between *fraction 1* and *2* and the number of N-phenyl succinimide units / oligomer determined by NMR spectroscopy are summarised in Table 1.

Table 1: Grafting yield (Y), ratios *fraction 1:2* and numbers of N-phenyl succinimide units per oligomer [a)]

Oligomer	Y [%]	ratio *fraction 1:2*	units / oligomer in *fraction 1* [b)]	units / oligomer in *fraction 2* [b)]	n_{av} [c)]
Eicosane	quant.	30:70	7.7	2.9	4.34
Squalane	quant.	31:69	8.6	2.6	4.46
TMN	quant.	21:79	8.3	1.8	3.16

[a)] molar ratio oligomer : monomer : Luperox 130 = 10 : 1 : 0.2
[b)] determined by NMR spectroscopy
[c)] average number of phenylsuccinimide units / oligomer

It can be seen that *fraction 1* contains graft products with longer side chains, in *fraction 2* short chains and single units are mainly found. As an average number of units per oligomer very similar results are obtained for eicosane and squalane (4.34 and 4.46, resp.), although squalane exhibits tertiary carbon atoms and dissimilar numbers of grafted units per oligomer could be expected. In the case of TMN a significantly lower number of units was obtained (3.16), indicating a higher reactivity of this oligomer towards grafting reactions compared with the less branched oligomers.

In a second series the amount of monomer was varied from 5 to 80%. NMR analysis of *fraction 2* showed approximately 2-3 units of monomer per oligomeric backbone for all three oligomers and all concentrations. *Fraction 1* was also analysed by SEC and UV spectroscopy. For UV analysis N-phenyl succinimide was synthesized [10] and a calibration curve in chloroform was determined.

In Table 2 grafting yields determined gravimetrically (*fraction 1+2*) are summarized and the number of phenyl succinimide units per oligomer in *fraction 1* obtained by SEC and UV analysis are compared with data from NMR spectroscopy.

Table 2: Yield (Y, *fraction 1+2*) and number of phenylsuccinimide units per oligomer in *fraction 1* determined by various methods

	Eicosane		Squalane		TMN	
Monomer	Y	units	Y	units	Y	units
[Mol%]	[%]	NMR/ SEC/ UV	[%]	NMR/ SEC/ UV	[%]	NMR/ SEC/ UV
5	quant.	7.6/ 5.1/ 8.9	quant.	8.9 / - / 6.3	quant.	8.0/ 5.7 / 6.8
10	quant.	7.7/ 5.4/ 8.5	quant.	8.6/ 6.6/ 6.3	quant.	8.3/ 6.2/ 6.1
20	93.3	7.7/ 6.4/ 10.4	96.8	8.5/ 6.7/ 6.8	96.9	8.8/ 6.1/ 7.4
40	57.5	-/ 6.6/ 10.6	71.6	-/ 6.6/ 7.2	73.9	-/ 6.5/ 16.1
80	15.9	-/ -/ 17.4	21.6	-/ -/ 6.7	16.3	-/ -/ 21.3

Tab. 2 shows that grafting yields are quantitative up to more than 10% monomer, above 20 mol% **1** homopolymer formation becomes significant. GC-analysis proved that the monomer had reacted completely. In the case of eicosane and TMN the numbers of phenylsuccinimide units per molecule oligomer show an increasing tendency when higher monomer concentrations are added. Grafting of squalane does not show any significant dependency on monomer concentration; further investigations are necessary to elucidate these results.

The influence of the monomer concentration on the amount of grafted oligomer was determined by GC analysis (Fig. 5).

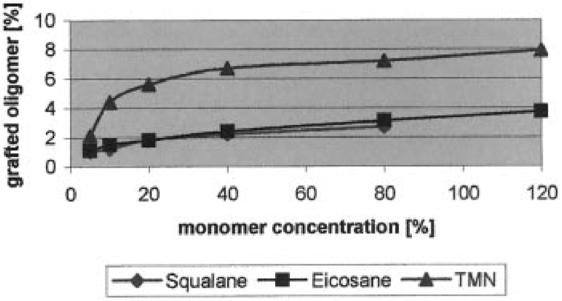


Fig. 5: Variation of monomer concentration

In Fig. 5 it can be seen that only for TMN the amount of grafted oligomer could be significantly increased by an increase of the monomer concentration up to 20%. In the case of eicosane and squalane the amount of grafted oligomer is much less influenced by the monomer concentration.

In order to check the influence of various reaction parameters experiments with different peroxide concentrations and reaction temperatures were conducted. It was found that the amount of modified oligomer could be slightly raised by increasing peroxide concentrations (Fig. 6) or reaction temperatures (Fig. 7).

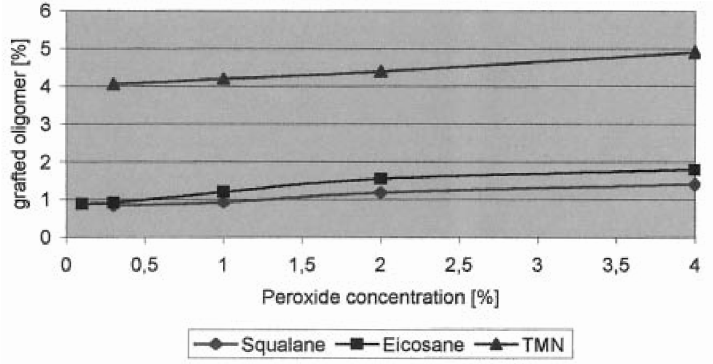


Fig. 6: Variation of peroxide concentration

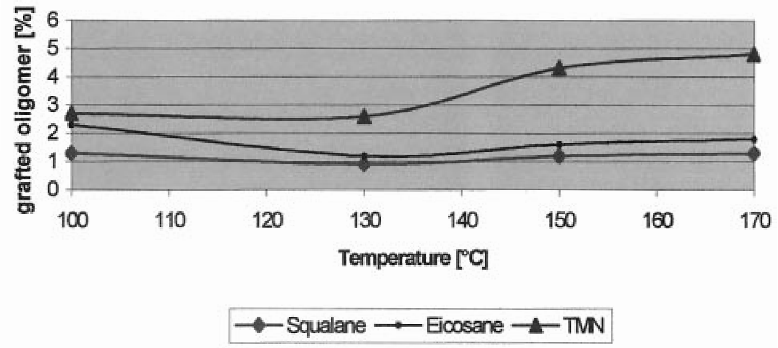


Fig. 7: Variation of reaction temperature

With 10 mol% maleimidobenzoic acid (**2**) lower grafting yields (70%) were obtained due to the restricted solubility. Nevertheless this functionalized maleimide (**2**) shows the same tendencies by variation of reaction parameters as depicted in Fig. 6 and 7 for the maleimide **1**.

Modification of polypropylene

Modification of PP (iPP FSC 4412, Borealis AG) was performed by reactive extrusion in a single screw extruder (Haake Rheocord 90, 3 heat zones + slot die) with **1** and Luperox130 as initiator (temperature program: 170 / 180 / 190°C, 100 rpm, average residence time 40-60 s).

Grafting yields were determined gravimetrically and by IR spectroscopy after reprecipitation in dichlorobenzene/petroleum ether. The monomer concentration was varied from 0.25 to 4 wt%, the initiator concentration from 0 to 1 wt%. Reaction parameters and grafting yields are summarized in Table 3.

Table 3: Grafting yields and reaction parameters for **1**-g-PP

1 [wt%]	Luperox 130 [wt%]	torque [Nm]	grafting yield [%]
-	-	24.0	-
-	0.5	19.5	-
0.25	0.5	22.0	76
0.5	0.5	18.0	92
1	0.5	16.0	94
2	0.5	12.0	88
4	0.5	9.5	77
1	-	21.5	5
1	0.1	21.0	64
1	0.25	17.0	89
1	0.5	16.0	94
1	1	12.5	91

It can be seen that grafting yields up to 94% could be achieved. Best results were observed with 1 wt% monomer as depicted in Figure 8; at higher concentrations inhomogeneous distribution was found to be the main problem.

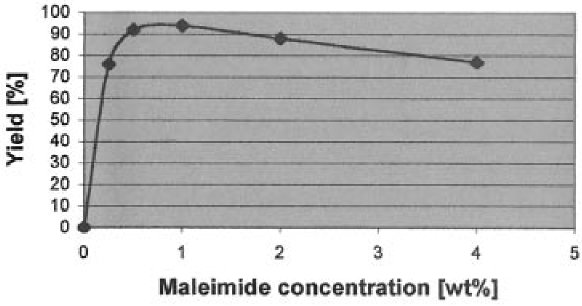


Fig. 8: Influence of the concentration of **1** on the grafting yield (0.5 wt% initiator)

In Figure 9 it can be seen that 0.5 wt% peroxide proved to be the optimum initiator concentration, at higher levels degradation of the polymer matrix was favoured, shown by MFI-measurements.

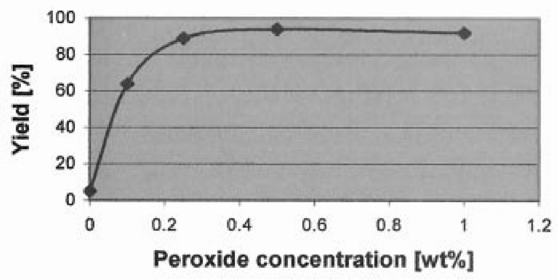


Fig. 9: Influence of the peroxide concentration (1 wt% of **1**)

DSC experiments of the modified samples indicated that cristallinity was not changed significantly; the mechanical properties of the polymer remained unchanged.

The same reaction conditions as mentioned above were used for experiments with maleimidobenzoic acid **2** and as a result the same dependency on monomer- and peroxide concentration was found. Grafting yields up to 93% were achieved with 1 wt% **2** and 0.5 wt% initiator. Due to the poor compatibility of **2** with the polymer significantly inhomogeneous samples were obtained above 2 wt% monomer.

Contact angle measurements of extruded sheets of **2**-g-PP were performed and the samples showed a significantly improved hydrophilicity. By adding 1 wt% of **2** the contact angle dropped from 109° for pure PP to 94°.

Conclusion

Maleimides **1** and **2** have been grafted successfully onto the oligomeric model compounds. Due to the facile isolation of graft products various analytical methods were elaborated. The most accurate analysis was obtained by NMR spectroscopy but also UV-spectroscopy as a much faster routine method gave similar results. It was shown that single units as well as short side chains were grafted onto the oligomers. Grafting yields were almost quantitative up to monomer concentrations of 20 mol%, at higher concentrations homopolymerisation became significant. The amount of oligomer which could be grafted was remarkably low; best results were obtained with TMN, eicosane and squalane showed a very similar reactivity.
Experiments with PP were performed by reactive extrusion and analysed by IR-spectroscopy. Compatibility of the aromatic monomer with PP was the main problem restricting grafting yields at higher monomer concentrations. Experiments with aliphatic maleimides are currently under investigation.

Acknowledgment

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