Surface and Bulk Modification of Polyolefins by Functional Aryl Nitrenes as Highly Reactive Intermediates

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Summary: Aromatic azides with hindered amine light stabilizer (HALS) residues or hydrophilic groups such as glucose, sucrose and dextrine residues were synthesized and used for surface modification of polyolefins. By UV-irradiation nitrenes were formed, which are able to react with polyolefin surfaces. By photochemical immobilization of the carbohydrates hydrophilicity of PE and PP was strongly increased (surface tensions > 44mN/m). Light stability of PP surfaces modified with HALS azides was comparable with PP, stabilised with Tinuvin 770. Bulk modification of ethylene-propylene and ethylene-octene copolymers was achieved by grafting nitrenes formed by thermal decomposition of azido benzoic acid. In a circulating air oven up to 1.55 wt% amino benzoic acid residues could be bonded covalently to ethylene-propylene-copolymers, less than half of it to ethylene-octene-copolymers. Reactive extrusion resulted in grafting yields of more than 50% for both types of copolymers.

Introduction

Polyolefins are limited in their application in several technologically important fields due to their low surface energy, lack of chemical functionalities, sensitivity to photo- or thermal oxidation and inadequate compatibility with other synthetic polymers. Accordingly, the chemical modification of polyolefins by grafting has been an area of intense interest as a route to improve these commodity polymers. The basic idea of our work was to test wether highly reactive intermediates such as nitrenes provide a useful method for polyolefin functionalization. For this purpose aromatic azides were used which are known to yield nitrenes by UV-irradiation as well as by heating [1]. These reactive intermediates can undergo a multitude of reactions, e.g. insertion into N-H, O-H and also C-H bonds, addition to olefines and proton abstraction reactions [2,3]. In a first step short-living, thermodynamically instable singlet nitrenes are formed, which can react with polyolefins, giving the corresponding amine (**I**) by insertion. By intersystem crossing (ISC) triplet nitrenes are obtained, which also can

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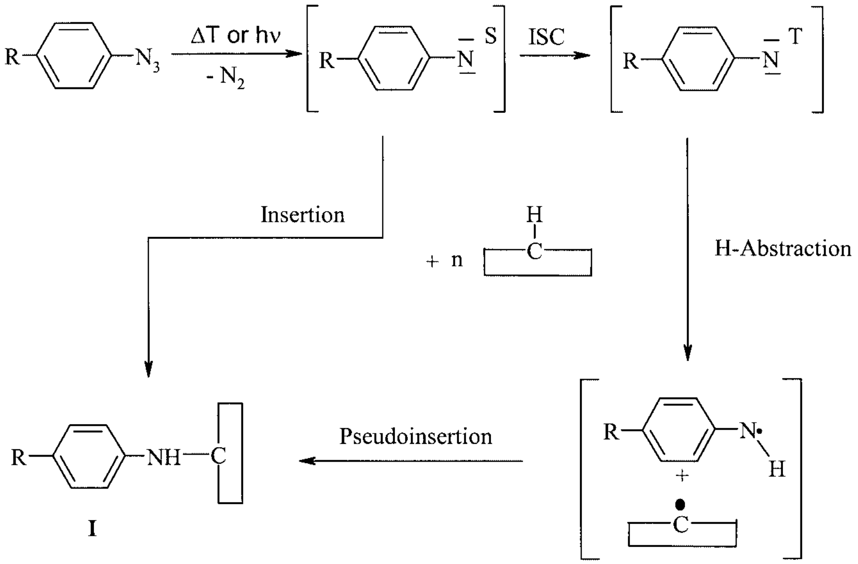
give the secodary amine (**I**) after H- abstraction and a so-called pseudo-insertion (Scheme 1). Due to the high reactivity of nitrenes a lot of byproducts can be formed, i.e. primary amines (R-Aryl-NH_2), oxidation products or diazocompounds.



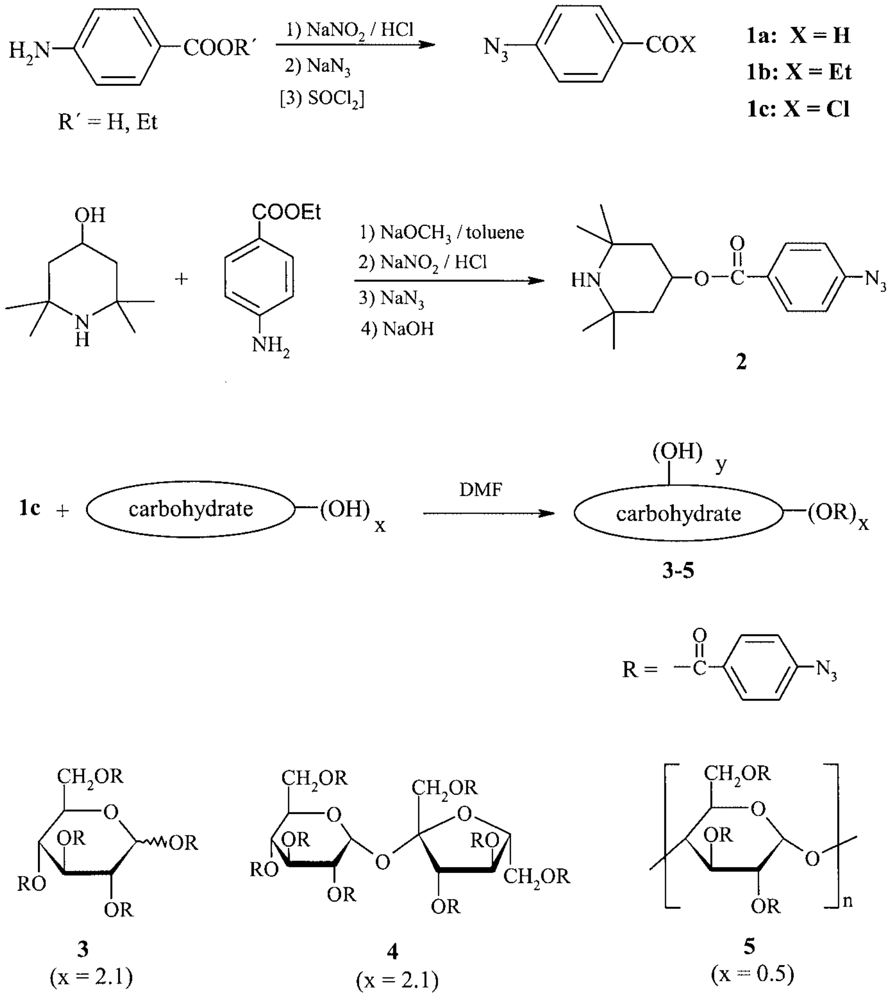
Scheme 1: Nitrene formation and (pseudo)insertion into C-H bonds

In this paper we summarize some of our recent work to increase the hydrophilicity and light stability of polyolefin surfaces by photochemical immobilization of azides with carbohydrate and hindered amine light stabilizer (HALS) residues and to achieve bulk modification by thermal immobilisation of aromatic azides.

Synthesis of functionalised aryl azides

4-Azidobenzoic acid (**1a**) and 4-azidobenzoic acid ethyl ester (**1b**) were synthesized by diazotation of 4-aminobenzoic acid (ethyl ester) and subsequent reaction with sodium azide [2]; 4-azidobenzoic acid chloride (**1c**) was prepared by reaction of **1a** with $SOCl_2$. The HALS derivative **2** was obtained by transesterification of 2,2,6,6-tetramethyl-4-piperidinol with 4-

aminobenzoic acid ethyl ester, subsequent diazotation, reaction with sodium azide and treatment of the hydrochloride of **2** with NaOH. The hydrophilic azides were prepared by reaction of 4-azidobenzoic acid chloride (**1c**) with glucose (**3**), sucrose (**4**) and dextrine (**5**) (Scheme 2).



Scheme 2: Synthesis of functionalized aryl azides

Surface modification of polyolefins

For covalent bonding of HALS residues onto polypropylene surfaces, PP films were immersed in 0.005-0.08 M solutions of **2** in toluene for 4-8 h. The dried polymers were irradiated with a high pressure mercury lamp (Heraeus TQ-150, 1 = 200-600 nm, distance lamp-polymer surface 15 cm, irradiation time 5-10 min). Unreacted azide and byproducts were removed by rinsing with various solvents. For comparison also **1b** was covalently bonded to PP using the same procedure. Real-time FT-IR spectroscopy was employed for monitoring the photolysis of the azides. Figure 1 shows, that after 1 min about 50% of **2** are decomposed and after 3 min there is no azide left.

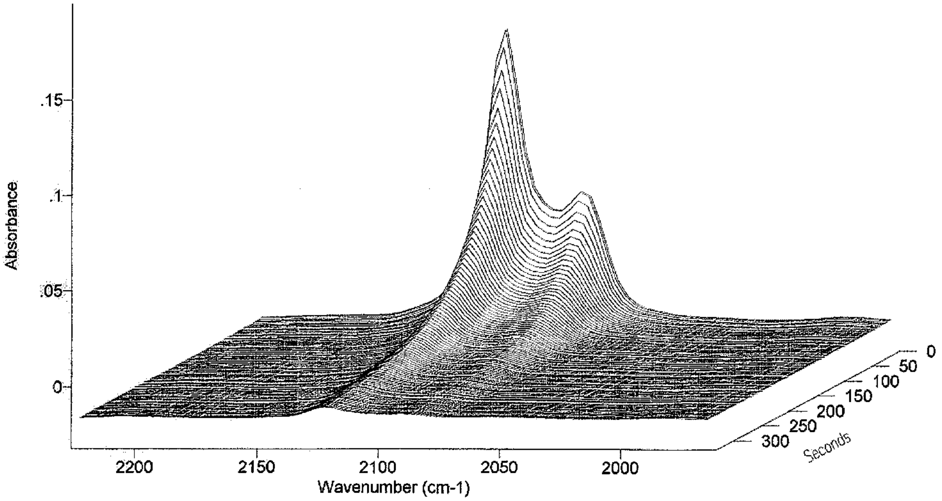


Fig. 1: Real time FT-IR spectrum of HALS azide **2**

Figure 2 shows FT-IR spectra of polypropylene, films with adsorbed azide **2** before irradiation and HALS-modified PP films after photolysis.

The covalent bonding of HALS residues was proved by the carbonyl band at 1718 cm^{-1} [Fig.2, (C)]. An evaluation of the percentage of immobilized azide compared with the amount of adsorbed azide showed that approx. 50% of the physically adsorbed azide were bonded to the polymer.

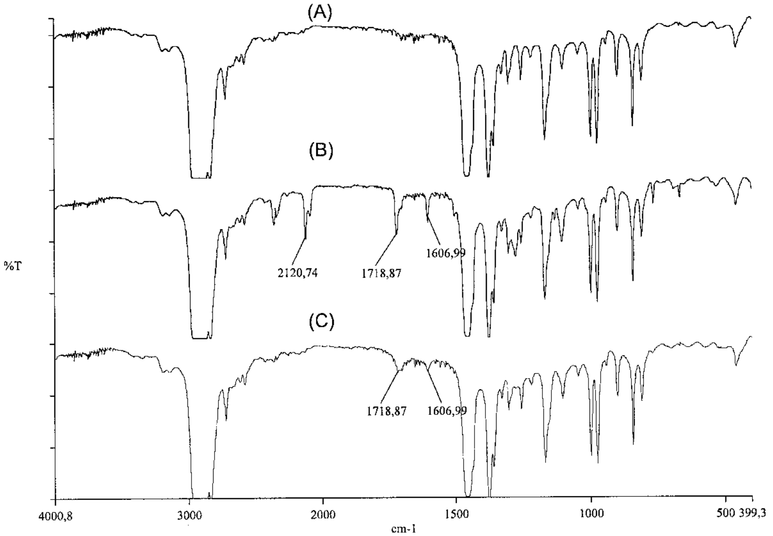


Fig. 2: FT-IR spectra of PP (A), PP + adsorbed **2** (B), and PP + covalentyl bonded **2** (C)

To increase the hydrophilicity of polyethylene and polypropylene surfaces polymer films were immersed in 0.02-0.05 M azide solutions for 2 h using ethanol (**1a**), acetic acid ester (**3**,**4**) and acetone:dioxane = 1:1 (**5**) as solvents. The dried polymers were irradiated for 5 min and the byproducts were removed by rinsing with i.e. acetone [4]. In one series polyethylene and polypropylene films were pretreated with a swelling agent (i.e. toluene) to enhance the diffusion of the azides **1a** and **3-5** and then immersed in the azide solutions .

Properties of the modified polymers

To determine the *light stabilizing efficiency* of the covalently bonded HALS-azide **2**, modified polypropylene films were irradiated for 400 h with the same high pressure mercury lamp used for the azide immobilisation and the relative increase of the carbonyl absorption was monitored by FT-IR spectroscopy. The carbonyl index A_{CO}/A_{CH3} was calculated from the intensity of the ester bands (1703-1732 cm^{-1}) and the bands at 2695-2752 cm^{-1}, characteristic of CH_3 groups and proportional to the amount of PP. For comparison films prepared with a commercial HALS (0.1 wt% Tinuvin 770$^{®}$), unstabilized samples and PP modified with **1b**, were also irradiated. The tests demonstrated that the light stabilizing efficiency of **2** is comparable to Tinuvin 770 (Figure 3).

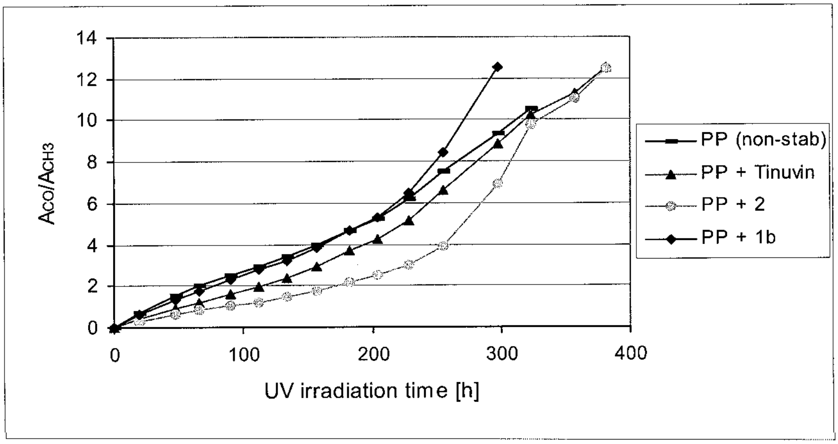


Fig. 3: Increase of carbonyl absorption versus irradiation time (initial A_{CO}/A_{CH3} subtracted)

The influence of the concentration of the azide solutions onto the stabilizing efficiency is shown in Figure 4.

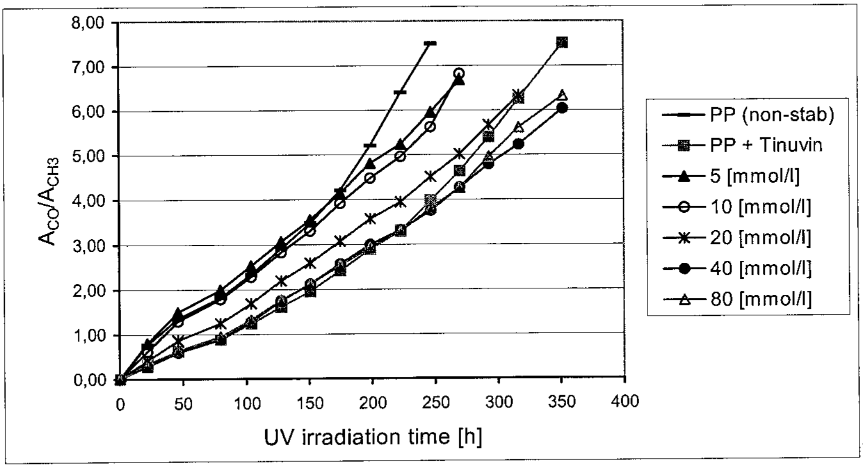


Fig. 4: Influence of azide concentration on photostabilizing efficiency of **2** (initial A_{CO}/A_{CH3} subtracted)

It can be seen that an increase of the concentration up to 40 mmol/l **2** yielded an enhancement of the light stabilizing effect, but a further increase up to 80 mmol/l did not improve the results, indicating a concentration equilibrium at the polymer surface.

The *hydrophilic properties* of polyethylene and polypropylene surfaces modified with the azides **1a** and **3-5** were investigated by contact angle measurements and special test inks (Arcotec®), available for polyolefins in a range from 30 to 44 mN/m. The results are summarized in Table 1 and 2.

Table 1: Contact angles [a] and surface tensions [b] of modified PP

azide	N_3-C_6H_4-COOR R =	solvent	pre-treatment	contact angle [°]	surface tension [mN/m]
1a	-H	ethanol	-	85	36
			toluene	75	40
3	glucose	acetic acid ester	-	74	40
			toluene	62	44
4	sucrose	acetic acid ester	-	70	42
			toluene	56	44
5	dextrine	acetone:dioxane (1:1)	-	56	44
			toluene	53	44

[a] contact angle of PP 90°, of a blank trial without azide 85°
[b] surface tension of PP 32 mN/m, of a blank trial without azide 34 mN/m

Table 2: Contact angles [a] and surface tensions [b] of modified PE

azide	N_3-C_6H_4-COOR R =	solvent	pre-treatment	contact angle [°]	surface tension [mN/m]
1a	-H	ethanol	-	80	38
			toluene	72	40
3	glucose	acetic acid ester	-	75	40
			toluene	62	44
4	sucrose	acetic acid ester	-	75	40
			toluene	60	44
5	dextrine	acetone:dioxane (1:1)	-	65	44
			toluene	63	44

[a] contact angle of PE 89°, of a blank trial without azide 84°
[b] surface tension of PE 34 mN/m, of a blank trial without azide 36 mN/m

By covalent attachment of **1a** and **3-5** without preswelling static contact angles decreased from 90° to 56-85° (PP) and from 89° to 65-80° (PE). Preswelling in toluene strongly increased the wettability in most cases and contact angles of 53-75° (PP) and 60-72° (PE) were obtained. Using the carbohydrate azides and a pretreatment step, surface tension was increased from 32 (PP) and 34 mN/m (PE) to ≥44 mN/m (PE, PP).

Bulk modification of polyolefins

Bulk modification of ethylene-propylene (Dutral CO 034®) and ethylene-octene copolymers (Engage 8200®) with **1a** ($T_{decomp.}$ 196°C) was achieved by heat treatment in a circulating air oven as well as by reactive extrusion. Grafting yields were determined by titration of the COOH-groups after purification of the modified polymers by reprecipitation.

In a first series polymer films were prepared from toluene solutions (1-5 wt% **1a**) and the samples were exposed to temperatures from 150 to 200°C for 10 min in a circulating air oven. The modified polymer films were significantly discoloured due to side reactions, i.e. the formation of diazo compounds by dimerisation of nitrenes. The main byproduct was found to be 4-aminobenzoic acid, formed by a second H-abstraction. All byproducts were removed by dissolving the samples in boiling toluene and precipitation with acetone. Grafting yields are summarized in Table 3.

An increase of the temperature from 150 to 200°C led to an increase of the grafting yields and with increasing amounts of azide the grafting yields decreased. After reprecipitation up to 1.55 wt% aminobenzoic acid residues could be bonded covalently to the polymer backbone. Grafting of Engage was less sucessful and temperatures of more than 150°C were necessary to modify this polymer due to the less reactive ethylene groups compared with the propylene residues in Dutral.

Grafting of Dutral in a twin-screw extruder (Berstorff; screw speed 100 rpm, 50-200°C, average reaction time 2 min) led to similiar results (57% grafting yield with 1 wt% **1a**), but grafting of Engage under the same conditions resulted in much higher yields than the modification in the circulating air oven. Grafting yields of 53% were obtained with 1 wt% **1a**, 40% with 2 wt% azide.

Table 3: Thermal immobilisation in a circulationg air oven

Temp.	**1a**	DUTRAL		ENGAGE	
[°C]	[wt%]	**1a** [wt%]+)	yield [%]	**1a** [wt%]+)	yield [%]
150	1	0.51	51	0	0
150	3	0.63	21	0.06	6
150	5	0.8	16	++)	++)
175	1	0.58	58	0.15	15
175	3	0.93	31	0.33	11
175	5	1.05	21	++)	++)
200	1	0.62	62	0.38	38
200	3	1.32	44	0.57	19
200	5	1.55	31	++)	++)

+) covalently bonded aminobenzoic acid
++) experiments not performed

Conclusion

Using thermal immobilisation of aromatic azides for bulk modification of polyolefins, grafting yields of more than 50% could be achieved, but due to by-products such as aromatic amines or diazocompounds reprecipitation was necessary. By photochemical immobilisation of aromatic azides with HALS or carbohydrate residues onto polymer surfaces, light stability as well as wettability of polyolefins could be significantly improved and by-products were removed easily by rinsing with solvents. Photolysis of aryl azides provides a useful route for surface modification of „difficult“ surfaces exhibiting no reactive centers such as polyolefins and chosing appropriate „active“ groups (i.e. bioactive groups, metal bonding groups...) „tailor-made“ surfaces are feasible.

Acknowledgment

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