polymer

Hydroboration/amination of EPDM with dicyclopentadiene as diene monomer

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Abstract

EPDM containing dicyclopentadiene (DCPD) as diene monomer was hydroborated with 9-borabicyclo(3.3.1)nonane (9-BBN). The subsequent amination with monochloroamine was expected to result in EPDM with primary amine groups. The conversion of the residual unsaturation of DCPD of EPDM was complete, but the chemical structure of the amine-modified EPDM could not be fully elucidated. Hydrogenated DCPD (DCPDH), the low-molecular-weight analogue of DCPD incorporated in EPDM, was also hydroborated and aminated and the resulting product was isolated and extensively characterized. It was shown to consist of DCPDH coupled to 9-BBN via the B-atom with an NH unit inserted in one of the B–C bonds of the 9-BBN unit. The product is in fact a zwitterion $RR'B^-(OH)NH_2^+R''$, which converts to the neutral $RR'BNHR''$ upon dehydration. Using the analytical data of the low-molecular-weight product it was deduced that a similar structure is present in the amine-containing EPDM. Surprisingly, both amine-modified EPDM and DCPDH reacted as primary amines; for example, in the presence of anhydrides imides were formed. Finally, application of the amine-containing EPDM resulted in compatible blends of EPDM with poly(styrene-*co*-maleic anhydride). © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

Impact modification of both amorphous and semicrystalline thermoplastics is usually achieved by dispersing a rubber phase in the thermoplastic matrix [1–5]. Thermoplastic/ rubber blends are prepared as reactor blends, such as ABS, AES and HIPS, or as melt blends, for example blends of PAs or polyesters with rubbers. In these blends the polarity of the thermoplastic and that of the rubber differ strongly, so compatibilization is necessary [6–9]. The compatibilizer of ABS, AES and HIPS is polymerized in a reactor: the formation of the graft onto the rubber occurs simultaneously with the formation of free polymer. For melt blends a block or graft copolymer is either prefabricated, which usually requires special polymerization technologies and is rather expensive [10], or it is formed during melt blending, i.e. *in situ* compatibilization. For the latter process the compatibilizer is usually formed from an elastomer with a chemical functionality reactive towards the thermoplastic [11,12]. Commercial examples are the application of maleic anhydride (MA)-modified EPM as *in situ* compatibilizer for PA/EP(D)M blends or elastomeric co- or terpolymers containing glycidylmethacrylate for polyester/polyolefin blends.

Poly(styrene-*co*-maleic anhydride) (SMA) with a relatively high MA content of 20–34 wt% has recently been introduced as a commercial material [13,14]. It is a thermoplastic which combines good flow properties, a relatively high glass transition temperature (145–180°C), a high dimensional stability, a good chemical resistance and a potential reactivity for further chemical modification or reactive blending. The presence of the rigid MA chain units results in a low chain flexibility and, thus, in a high molecular weight between entanglements (~ 20 kg mol^{-1}) [13] and in a moderate impact toughness [15]. Blending of SMA with a rubber will result in increased impact toughness. Blends of SMA with ABS were developed for this purpose, but these do not have optimum u.v. and oxidative stability because of the unsaturated polybutadiene phase of ABS. EP(D)M would be a better choice as impact modifier, at least if SMA/EP(D)M blends can be compatibilized. The high reactivity of cyclic anhydrides of SMA towards primary amines [16] suggests that EP(D)M with primary amine functionalities is a suitable compatibilizer for SMA/EPDM blends.

Several routes have been developed for the preparation of

amine-containing polyolefins. A diene monomer with an amine group can be introduced during the polymerization of EPDM in the presence of a surplus of Ziegler Natta catalyst [17,18]. The surplus of catalyst acts as a protecting agent for the amine and as a result the amine group does not interfere with the polymerization. Primary amine-modified EPDMs prepared in this way were shown to be very effective compatibilizers for blends of SMA with polyolefins [19–21]. However, it is obvious that the large amounts of catalyst needed will result in a rather expensive product. Dimethylaminoethyl methacrylate and *t*-butylaminoethyl methacrylate have successfully been grafted onto a variety of polyolefins [22–28], but since tertiary and secondary amines, respectively, are used, the compatibilization in blends with SMA was not optimum[29,30]. EPM-g-MA can be modified with suitable diamines, preferably containing one primary and one secondary amine, such as 3-amino-1-methylaminopropane [31–34]. The primary amine preferably reacts with EPM-g-MA and, as a result, the residual amine of the functionalized EPM has a secondary structure, which again may not be optimum for blending with SMA.

An elegant route for obtaining modified polyolefins is the hydroboration route as developed by Chung. An ω-alkenyl-borane, i.e. a hydroborated diene monomer, is introduced during Ziegler Natta polymerization of PP [35–41]. Alternatively, PP or EPM containing a diene monomer such as 1,4-hexadiene is hydroborated [40–43]. The hydroborated polyolefin is subsequently converted by oxidation with hydrogen peroxide in a basic medium to hydroxyl-containing polymers or used for graft polymerization of
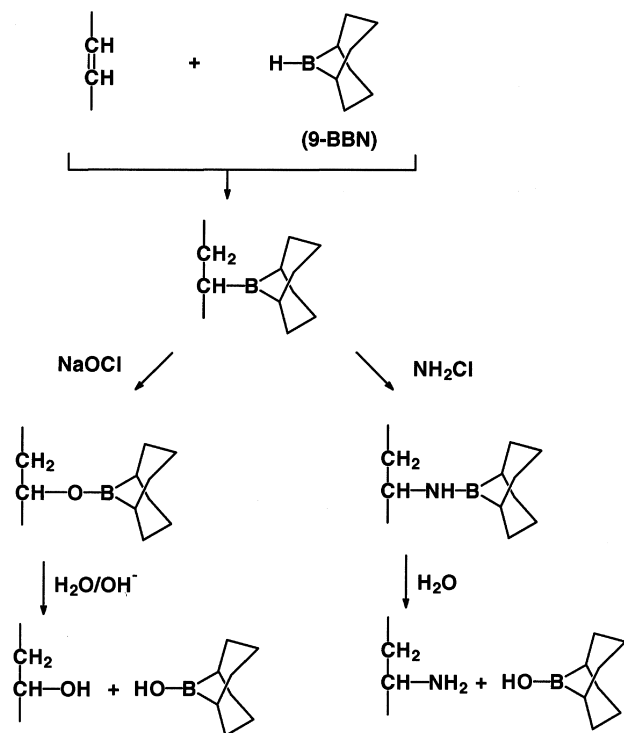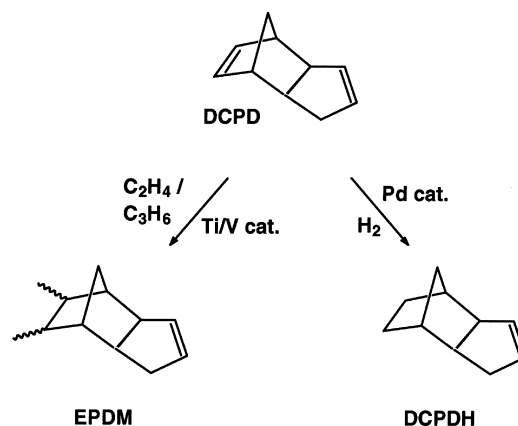

Fig. 2. Hydrogenated dicyclopentadiene (DCPDH) as a representative low-molecular-weight model for dicyclopentadiene (DCPD) incorporated in an EPM chain.

poly(methyl methacrylate) onto the polyolefin. Brown and co-workers have shown that hydroboration of low-molecular-weight olefins followed by hydration or amination yields alcohols or amines [44–46]. The chemical mechanism of the hydroboration and the subsequent modification is depicted in Fig. 1 with 9-borabicyclo(3.3.1)nonane (9-BBN) taken as a typical borane. 9-BBN adds to the unsaturation. Next the C–B bond formed is oxidized to a C–O–B structure, which is cleaved in the presence of water, resulting in hydroxyl groups C–OH. The hydroborated olefin may also be treated with monochloroamine (NH_2Cl). The C–B bond is then converted to a C–NH–B unit, which can be hydrolysed to a primary amine $C-NH_2$.

The goal of the present study was to prepare a primary-amine-containing EPDM with dicyclopentadiene (DCPD) as diene monomer (Fig. 2) via the hydroboration/amination route. In the first instance, the chemical structure of the amine-modified EPDM could not be fully elucidated, so we carried out a parallel study with hydrogenated DCPD (DCPDH) as a low-molecular-weight model (Fig. 2). The characterization of the reaction product formed from DCPDH was of great help in the analysis of the amine-modified EPDM. An extended version of the reaction scheme in Fig. 1 will be used to explain the unexpected structures of the amine-containing DCPDH and EPDM formed. Subsequently, the reactivity of the modified EPDM and model substrate was studied.

2. Experimental

2.1. Synthesis

For improved solubility and analytical sensitivity the modification of EPDM was first carried out with a low-molecular-weight EPDM with a high DCPD content: Trilene® 65 (Uniroyal) with 9.5 wt% DCPD and a number-average molecular weight of 7.0 kg mol^{-1}. In a

Fig. 1. Mechanism of hydroboration and subsequent hydration or amination of an olefin [44–46].

typical example 53.6 g EPDM was dissolved in 100 ml toluene and the solvent was evaporated under reduced pressure to eliminate traces of oxygen and water. The EPDM was then dissolved under nitrogen in 300 ml of tetrahydofuran (THF), which was dried via distillation over calcium hydride. Monofunctional 9-BBN was used to avoid gel formation that could be caused by reaction of the polyfunctional EPDM with di- or trifunctional boranes. A 9-BBN solution (90 ml, 0.5 M) in THF was added to the polymer solution under dry nitrogen. The temperature was raised to 50°C and the solution was stirred for 2 h. After cooling to ambient temperature, first 20 ml of a 10 M ammonium hydroxide solution and then 400 ml of a 2 M sodium hypochlorite solution were added with vigorous agitation. Both the ammonium hydroxide and hypochlorite solutions were deoxygenated by passing a stream of nitrogen through them before addition to the hydroborated polymer solution. The temperature of the stirred solution was raised to 50°C and after 6 h the polymer was recovered by precipitation in methanol and drying under vacuum. In a similar procedure a high-molecular-weight EPDM was modified: Keltan® 520 (DSM): 4.5 wt% DCPD with a number-average molecular weight of about 35 kg mol^{-1}.

DCPDH was obtained by selective hydrogenation of the endocyclic unsaturation of commercial endo-DCPD. DCPD (95.4 g) and a carbon black-supported palladium catalyst (5.2 g, 5 wt% Pd) were introduced into a 160 ml autoclave, which was stirred at 500 rev min^{-1}. After deoxygenation of the mixture by purging with nitrogen three times, the reactor was pressurized with hydrogen and heated to about 70°C. The pressure was kept constant by continuous hydrogen supply. The hydrogenation was continued until hydrogen uptake decreased. The product was isolated by filtering off the heterogeneous catalyst.

The hydroboration/amination of DCPDH was carried out in a similar way to that described above for EPDM. DCPDH (5.8 g) was dissolved in 50 ml dry THF, 100 ml of the 9-BBN solution in THF was added and after hydroboration a tenfold excess of the 10 M ammonium hydroxide solution and of the sodium hypochlorite solution were added. The THF solution was separated from the aqueous phase and washed with a 0.5 M sodium hydroxide solution and stored at 4°C. The crystalline product was filtered off and dried under vacuum at 60°C.

2.2. Modification

A fivefold molar excess of phenylisocyanate was added to a solution of amine-modified EPDM in dry THF. The solution was refluxed for 6 h. The polymer was recovered in methanol, reprecipitated from a THF solution in methanol and dried under vacuum. The amine-modified EPDM was also reacted with a twofold excess of phthalic anhydride in toluene at 75°C for 4 h. The product was precipitated in methanol and analysed before and after drying for 1 h at 180°C under vacuum.

Blends of the amine-containing EPDM were prepared with SMA containing 28 wt% MA: Stapron® S SMA SZ28110 (DSM). Films were cast from homogeneous THF solutions of the amine-modified low-molecular-weight EPDM and SMA. In addition, SMA/EPM/amine-modified EPDM (45/35/20; w/w/w) blends were prepared in a home-built mini-extruder at 260°C. The mini-extruder is a small-scale, fully intermeshing, conical, corotating twin-screw extruder with a recirculation channel, allowing its use as a batch mixer with a capacity of 5 g. Polymer strands are rapidly ejected from the mixing chamber by opening a release valve.

The thermal stability of the amine-containing DCPDH was studied by heating at various temperatures. Modification with phthalic anhydride was performed by first dissolving a 1:1 molar mixture of the modified DCPDH and phthalic anhydride in THF and then heating the mixture at various temperatures in the solvent and after evaporation of THF.

2.3. Characterization

Fourier transform infrared (*FT*i.r.) spectra were recorded on Perkin-Elmer 1600 or 1720X *FT*i.r. spectrometers. Films of the (modified) EPDM of 0.1 mm or less were prepared either by pressing in a hot press at about 200°C or by solvent casting on sodium chloride plates. The DCPDH (derivatives) were mixed with potassium bromide and pressed into pellets. In some cases a Bruker *FT*i.r. microscope was used. ^{1}H, ^{11}B and ^{13}C nuclear magnetic resonance (n.m.r.) spectra were recorded on Bruker AC 200 or Varian Unity 300 n.m.r. spectrometers. Boric acid was used as reference for ^{11}B n.m.r. The (modified) low-molecular-weight EPDM and the DCPDH (derivatives) were dissolved in CDCl$_3$ at room temperature, whereas the modified high-molecular-weight EPDM was dissolved in C$_2$D$_2$Cl$_4$ at 125°C.

Gas chromatography/mass spectroscopy (g.c./m.s.) and probe m.s. were performed on DCPDH (products) using Finnegan 4600 or Kratos MS80 mass spectrometers. For pyrolysis/g.c./m.s. a Finnegan 4600 mass spectrometer was used. C and H contents were determined with a Heraeus Rapid CHN Element Analyser, N content with a LECO FP Analyser and B content with a Fisons Instruments ICP after digestion of samples in an acid environment in a closed container. Elemental analysis of the modified, high-molecular-weight EPDM was performed before and after extracting samples under reflux with methanol or toluene/methanol (25/75 v/v). E.s.c.a. measurements were performed on a Leybold MAX200 photoelectron spectrometer (Mg Kα radiation; 13.0 kV and 20.0 mA).

The reaction product of DCPDH was studied by thermogravimetric analysis (t.g.a.)/m.s. For t.g.a. a Perkin-Elmer TGS-2 mass balance and for m.s. a Balzers QMS 420/QME 112 mass spectrometer were used. The t.g.a./m.s. interface was developed within DSM Research[47]. The molecular structure of the amine-modified DCPDH was fully

elucidated with X-ray diffraction of a single crystal (0.5 × 0.4 × 0.3 mm) after recrystallization from methanol[48]. Data were collected on an Enraf–Nonius CAD4F diffractometer with Zr-filtered Mo Kα radiation. The space group is $P2_1/n$ and the cell dimensions are $a = 16.771(2)$, $b = 6.8819(5)$ and $c = 17.039(1)$ Å with $\beta = 111.502(7)°$. There is one molecule in the asymmetric unit. The final R factor amounts to 0.064 for 2041 observed reflections.

Gas permeation chromatography (g.p.c.) of the (modified) low-molecular-weight EPDM was run on a Hewlett Packard 1090 HPLC equipped with four Polymer Laboratories PL gel columns (10^5, 10^3, 500 and 100 Å) with THF as eluent (1 ml min^{-1}) at 45°C with a variable wavelength diode array detector and a Hewlett Packard 1037 refractive index detector. Apparent molecular weights were determined on the basis of PS calibration. Transmission electron micrographs were obtained of cryo-coupes of thickness 100 nm after staining with ruthenium tetroxide vapour using a Philips CM200 microscope (120 kV).

3. Results and discussion

3.1. Synthesis and preliminary characterization of amine-modified EPDM

The hydroboration reaction proceeded smoothly and was completed at room temperature within a few hours. The ^{1}H n.m.r. spectrum of the low-molecular-weight EPDM with 9.5 wt% DCPD before reaction showed two signals at 5.5 and 5.6 ppm, characteristic of the two H-atoms of the residual, exocyclic unsaturation. At 2.5 and 3.0 ppm the corresponding allylic H-atoms resonate. After reaction with a stoichiometric amount of 9-BBN these four ^{1}H n.m.r. signals disappeared, indicating that the unsaturation was completely converted upon hydroboration. New ^{1}H n.m.r. signals appeared in the 3–5 ppm region. Less than one equivalent of 9-BBN gave mixed hydroborated and unreacted diene monomer along the EPM chain. The hydroboration could be performed in THF as well as in aliphatic hydrocarbon solvents.

The reaction between ammonium hydroxide and sodium hypochlorite in water generates NH$_2$Cl[49], which has only a limited stability. Therefore, NH$_2$Cl was produced *in situ*. In THF solution the conversion of the hydroborated EPDM took place much faster than in two-phase heptane/THF mixtures. It is very important to have complete conversion of all 9-BBN units attached to EPDM. Because of the ease with which these groups react with oxygen and form reactive radical intermediates, crosslinked products are readily formed. The 3–5 ppm region of the ^{1}H n.m.r. spectrum of the amine-modified EPDM differed from that of the hydroborated EPDM. Two new signals at 3.4 and 4.5 ppm were observed. The N content of the purified product was 0.9 wt%, which agrees with complete conversion of the unsaturation of the 9.5 wt% DCPD present

in the low-molecular-weight EPDM into an equivalent of amine. E.s.c.a. demonstrated the presence of C (97.4 atom%) and small amounts of O, N, B, Si and S (1.0, 0.5, 0.5, 0.5 and 0.1 atom%, respectively). The e.s.c.a. peak at 398.6 eV is the N(1s) line, characteristic of an amine. The peak at 101.8 eV is a Si(2p) line, probably due to silicon oil contamination. The origin of sulfate and/or sulfite, as evidenced by the typical S(2p) line at 167.2 eV, is not clear. The detection of oxygen is fully explained by the presence of silicone oil and sulfate and/or sulfite. It was first thought that the presence of B was due to contamination with a 9-BBN reaction product.

A solution of the amine-modified EPDM in chloroform quickly gelated upon addition of traces of acid. Due to the formation of ammonium-modified EPDM, ionic clustering of the polymer chains will give rise to a physically crosslinked network. Addition of a strong base restored a low viscosity solution.

In summary, the hydroboration and subsequent amination of EPDM with DCPD as diene monomer proceeded smoothly, the conversion of the residual unsaturation of DCPD was complete and the formation of an equivalent of amine was demonstrated. Unfortunately, we were not able to finish the study at this stage, since the chemical structure of the modified EPDM could not be fully elucidated. This is a familiar problem with chemically modified polymers. The amount of the introduced chemical functionalities is often small in relation to the detection limits of spectroscopic techniques, such as i.r. and n.m.r. To fully characterize the chemical structure of the amine-modified EPDM, a parallel study was performed on hydroborated/aminated DCPDH, a representative low-molecular-weight model for DCPD incorporated in EPDM (Fig. 2). This model study allowed a more detailed characterization using other analytical techniques, such as m.s. and X-ray diffraction. Subsequently, the analytical results for the modified low-molecular-weight model were used to further characterize the amine-modified EPDM.

3.2. Synthesis and characterization of amine-modified DCPDH

^{1}H n.m.r. spectroscopy showed that upon hydrogenation of DCPD, besides the monosaturated DCPDH (81 mol%), the double saturated species (DCPDHH: both endo- and exocyclic unsaturations of DCPD have been hydrogenated; 19 mol%) is formed as well. G.c./m.s. showed 87 area% DCPDH, 11 area% DCPDHH and 2 area% residual DCPD. No attempt was made to reduce the amount of DCPDHH by optimizing the hydrogenation time and/or conditions, since DCPDHH will behave as an inert diluent during hydroboration.

The hydroboration of DCPDH proceeded smoothly. *FT*i.r. of the unpurified product showed the disappearance of the 3040 cm^{-1} peak, which is characteristic of the DCPDH unsaturation, indicating a high conversion of the

unsaturation. I.r. and g.c./m.s. did not provide straightfor-ward structural information on the hydroborated DCPDH. No attempt was made to fully characterize this intermediate.

*FT*i.r. showed that upon amination the hydroborated DCPDH intermediate was completely converted. New peaks were observed at 1600 cm^{-1} and between 3100 and 3600 cm^{-1}. The ^{1}H and ^{13}C n.m.r. spectra of the crystalline material, obtained after cooling the THF solution, were very complex. This is probably due to the presence of isomers and the overlap of a large number of peaks of similar but non-equivalent ^{1}H- and ^{13}C-atoms, respectively. The con-version of the unsaturation of DCPDH was complete, since the characteristic ^{1}H n.m.r. signal at 5.4 ppm and ^{13}C n.m.r. signals at 130 and 133 ppm have disappeared.

G.c./m.s. of the unpurified aminated DCPDH showed the presence of two main components, which are thought to be isomers, since the molecular weight of both was 271 g mol^{-1}, the fragmentation patterns were similar and the molar intensity was about 1:1. The molecular weights of these two isomers differ from that of the expected, primary-amine-modified DCPDH ($C_{10}H_{17}N$: 151 g mol^{-1}). The exact molecular weight was determined with probe m.s. in combination with electric ionization and was shown to be 271.247 g mol^{-1}. This value agrees with a bruto formula of $C_{18}H_{30}BN$ (calculated: 271.247 g mol^{-1}). The exact mol-ecular weight of one of the major fragmentation products was determined as 136.130 g mol^{-1}, which agrees with 136.130 g mol^{-1} calculated for $C_8H_{15}BN$. This fragmenta-tion product suggests that upon amination the amine group is incorporated in the 9-BBN unit instead of in between the DCPDH and 9-BBN moieties. The presence of isotope peaks with a ratio of about 4:1 for both the molecular weight ion and the fragmentation products confirms the presence of B (^{11}B:^{10}B; 80:20). On the basis of these m.s. data the for-mation of the expected primary-amine-containing DCPDH as the main product can be excluded and the formation of an amine-containing DCPDH/BBN coupling product is suggested.

G.c./m.s. of the raw material in THF also showed two isomers with a molecular weight of 152 g mol^{-1} as two minor components. The g.c./m.s. characteristics of these two products are identical to those of hydroxyl-modified DCPDH ($C_{10}H_{16}O$), which were obtained in a separate experiment by treatment of hydroborated DCPDH with NaOCl in the presence of air (see Fig. 1). For less than 5 area% a component with a molecular weight of 151 g mol^{-1} was detected, which does agree with the expected primary-amine-containing DCPDH. As expected, the inert DCPDHH is identified.

Pyrolysis/g.c./m.s. of the hydroborated/aminated DCPDH showed that it did not pyrolyse, but just evaporated in the pyrolysator. The molecular weight ion at $m/e = 271$ g mol^{-1} was observed together with typical fragmentation peaks at 203 and 136 g mol^{-1}. The fragmentation peak at $m/e = 203$ g mol^{-1} may be attributed to an amine-containing DCPDH/9-BBN coupling product with the DCPDH unit

degraded via a retro-Diels–Alder reaction, resulting in cyclopentadiene and $C_{13}H_{24}BN$. The second fragmentation peak at $m/e = 136$ g mol^{-1} was also observed with g.c./m.s. and is attributed to $C_8H_{15}BN$, i.e. a 9-BBN moiety including an amine.

The ^{11}B n.m.r. spectrum of the amine-modified DCPDH was dominated by a broad ^{11}Bn.m.r. signal, due to the pre-sence of boron in the glass parts of the n.m.r. probe. Super-imposed on this signal a large and sharp signal at 50 ppm was observed and two very small peaks at 38 and 22 ppm (less than 5 mol% of the total amount of B present in the modified DCPDH). After acidification of the n.m.r. solution with trifluoroacetic acid the 50 ppm peak disappeared. The peak at 10 ppm showed an increase in intensity, whereas the one at 38 ppm was not affected. The chemical shift of the main ^{11}B n.m.r. signal 50 ppm upfield from the reference peak of tricoordinated ^{11}B in the boric acid reference suggests that the corresponding species contains a tetra-coordinated ^{11}B. The spectral changes upon acidification indicate a change from tetra- to tricoordinated B, a change that resembles the change from anionic borate $[B(OH)_4^-]$ to neutral boric acid $[B(OH)_3][50]$. Thus, in solution the amine-containing DCPDH/9-BBN adduct is actually present as a species with a tetracoordinated B in equilibrium with a small amount of a substance having a tricoordinated B.

Elemental analysis of the amine-modified DCPDH after recrystallization showed the following composition (in wt%): C, 72.7; H, 11.2; B, 3.3; N, 4.6. The molar B:N ratio is 0.93:1. The composition of the recrystallized product deviates significantly from the calculated one for $C_{18}H_{30}BN$ (in wt%): C, 79.7; H, 11.0; B, 4.1; N, 5.2. T.g.a./m.s. showed that water was lost in two steps upon heating from room temperature to about 150°C. The total water content was 8.0 wt%, which is somewhat more than one water molecule of hydration for each $C_{18}H_{30}BN$ molecule (6.2 wt%). Taking the experimentally determined amount of water into account the calculated elemental composition for $C_{18}H_{30}BN\cdot1.3H_2O$ is (in wt%): C, 73.4; H, 11.0; B, 3.8; N, 4.8, which agrees rather well with the experimental composition.

The molecular structure as determined with X-ray dif-fraction[48] after recrystallization in methanol is $C_{18}H_{32}BNO\cdot CH_3OH$ (Fig. 3). The molecular structure corresponds to a zwitterionic RR′B$^-$(OH)NH$_2^+$R″ moiety. Obviously, the product does not contain the expected primary amine, but a secondary amine, which is not inserted in the B–C bond between the DCPDH and the 9-BBN moieties, but in one of the B–C bonds of 9-BBN itself. The amine-containing DCPDH/9-BBN adduct is in the *endo* form, like the original DCPDH. The presence of the methanol molecule in the X-ray diffraction molecular struc-ture is an artefact of the recrystallization procedure. During g.c./m.s. and pyrolysis/g.c./m.s. the RR′B$^-$(OH)NH$_2^+$R″ moiety probably converts to RR′BNHR″ with loss of water, as was already evidenced by t.g.a./m.s. As a result, m.s. results in the observation of $C_{18}H_{30}BN$ instead of
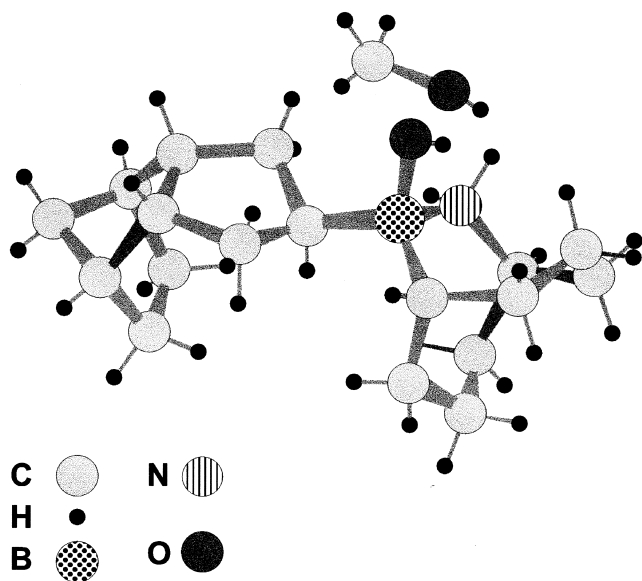
Fig. 3. Molecular structure of the crystalline product with the bruto formula $C_{18}H_{32}BNO \cdot CH_3OH$, obtained by hydroboration and subsequent amination of hydrogenated dicyclopentadiene.

$C_{18}H_{32}BNO$. The ^{11}B n.m.r. spectrum of the amine-modified DCPDH in solution indicates a negatively charged, tetracoordinated B atom, which agrees with the $RR'B^-(OH)NH_2^+R''$ unit, which is in equilibrium with a neutral, tricoordinated B atom in the corresponding $RR'BNHR''$ unit.

3.3. Characterization of amine-modified EPDM

It was already shown that upon hydroboration/amination of EPDM with DCPD as diene monomer the conversion of the unsaturation was complete and that indeed a stoichiometric amount of amine was formed. The results of the characterization of the amine-modified low-molecular-weight model DCPDH were used to further characterize the modified EPDM. The analyses were performed on a modified, high-molecular-weight EPDM with 4.5 wt% DCPD.

Elemental analysis showed that besides the expected N of the amine B was also present in the modified EPDM. The N content was 0.51 wt% (± 0.03) and the B content was 0.35 wt% (± 0.01). Extraction of the modified EPDM with refluxing methanol or methanol/toluene did not affect the N and B contents. Hence, the N and B are probably chemically bound to the amine-modified EPDM. The molar B/N ratio is 0.89, which roughly agrees with the $C_{18}H_{30}BN$ structure demonstrated for the amine-modified DCPDH (Fig. 3). The experimental N and B contents are within experimental error of the contents calculated for complete conversion of the residual unsaturation of DCPD (N, 0.48 wt%; B, 0.37 wt%).

The e.s.c.a. data of the amine-containing EPDM for N and B are also in agreement with the structure in Fig. 3. The B:N atom ratio is 1:1. The e.s.c.a. B(1s) line at 190.1 eV

is typical of organic B, the N(1s) line at 398.6 eV is typical of an amine and not of an ammonium. Probably, the high vacuum applied during the e.s.c.a. measurement results in dehydration and conversion of the ammonium in $RR'B^-(OH)NH_2^+R''$ to the amine in $RR'BNHR''$.

Besides the broad background signal of glass in the n.m.r. probe, the ^{11}B n.m.r. spectrum of the modified EPDM showed the same three peaks as observed for the modified DCPDH, namely a very strong one at 50 ppm and two minor ones at 38 and 22 ppm (less than 5 mol%). This also indicates that the amine-modified EPDM contains a structure which is similar to that of the amine-modified DCPDH (Fig. 3).

The pyrolysis/g.c./m.s. chromatogram of the aminated EPDM was very complex, mainly due to the large number of m.s. peaks derived from the EPM backbone. The characteristic DCPD fragment of unmodified EPDM with $m/e = 132$ g mol^{-1} was not detected. Scanning on $m/e = 136$ g mol^{-1}, which corresponds with the fragmentation product consisting of a 9-BBN unit with the amine incorporated ($C_8H_{15}BN$), one pyrolysis product with $m/e = 205$ g mol^{-1} and two products with $m/e = 203$ g mol^{-1} were identified. The mass spectra of these three species showed the typical isotope pattern of $^{11}B{:}^{10}B$. The mass spectra of the two components with $m/e = 203$ g mol^{-1} closely resembled that of one of the pyrolysis products of the amine-containing DCPDH and probably correspond with the structure in Fig. 3 with one molecule of cyclopentadiene split off via a retro-Diels–Alder reaction. The species with $m/e = 205$ g mol^{-1} probably corresponds to a similar but saturated structure, but containing an unsaturation.

The presence of B and N in a 1:1 molar ratio in the amine-modified EPDM, as demonstrated by elemental analysis and e.s.c.a., the close resemblance of the ^{11}B n.m.r. spectrum, and especially of the pyrolysis g.c./m.s. data of the modified EPDM to the corresponding spectrum and data of the modified DCPDH strongly indicate that the amine-modified EPDM contains the structure as depicted in Fig. 3.

3.4. Mechanism of hydroboration/amination of DCPDH and DCPD-containing EPDM

In Fig. 4 an extended version of the hydroboration/ amination reaction scheme of Fig. 1 is given. Hydroboration of DCPDH and EPDM containing DCPD as diene monomer with 9-BBN probably results in addition of the 9-BBN unit to the least sterically hindered unsaturated C atom. By analogy with the hydroboration/hydrolysis of PP and EPDM with 1,4-hexadiene as diene monomer, it was expected that the amine would insert in the B–C bond between the 9-BBN and the DCPDH moieties[35–41]. However, the various chemical analyses for the amine-modified DCPDH and EPDM have shown that this expected product is not formed here. The amine is in fact inserted in one of the two B–C bonds of the 9-BBN unit itself. It has been suggested that stereo-electronic factors may result in such an
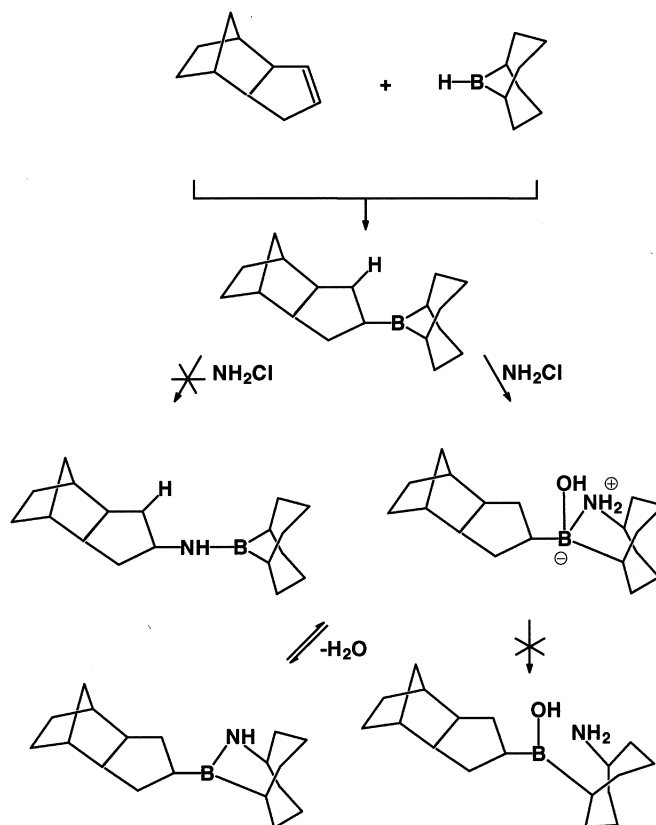
Fig. 4. Reaction mechanism of hydroboration and amination of hydrogenated dicyclopentadiene and EPDM with dicyclopentadiene as diene monomer; the product with the primary amine was expected from refs [44–46], whereas the amine-containing DCPDH/9-BBN was actually formed.

unexpected insertion [51]. Probably the bulky DCPD(H) unit screens the B–C bond between the *endo* cyclopentane ring of DCPD(H) and the 9-BBN moiety. For PP and EPDM with 1,4-hexadiene as diene monomer there will be much less steric hindrance for the B–C bond between 9-BBN and 1,4-hexadiene. Besides the unexpected insertion of the amine in the 9-BBN ring, it is noteworthy that the subsequent hydrolysis to primary amine did not take place. The close proximity of the B–OH and C–NH_2 groups that are expected to be formed upon hydrolysis (Fig. 4) probably explains the fast reformation of the B–C bond as in the original species.

3.5. Modification and blending of amine-modified EPDM

The amine-modified EPDM was reacted with phenylisocyanate and g.p.c. chromatograms were recorded with tandem u.v. and RI detection. The u.v. absorption at 254 nm of the phenylisocyanate-modified EPDM is similar to the RI trace of the neat EPDM. This indicates that the amine-modified EPDM can react with isocyanates without the occurrence of branching, crosslinking or degradation. In addition, it shows that the DCPD content of the original EPDM is independent of the molecular weight.

*FT*i.r. of the amine-modified EPDM reacted with phthalic anhydride at 75°C showed that a new species was formed with i.r. bands at 1650 and 1710 cm^{-1}. These are typical of an amic acid, although the vibration at 1550 cm^{-1} was not observed. Heating the product to 180°C resulted in a change in the i.r. spectrum. Now an intense peak at 1710 cm^{-1} and a smaller one at 1780 cm^{-1} were visible, which are characteristic of a cyclic imide derived from a primary amine. Thus, it is suggested that although the amine-modified EPDM does not contain a primary amine but a protonated secondary amine instead, it reacts as a primary amine in the presence of anhydride.

A blend of SMA and amine-modified, low-molecular-weight EPDM was prepared by dissolving the polymers in THF and then evaporating the solvent. The film that was obtained was transparent, indicating a sub-micron morphology and thus a very effective *in situ* compatibilization. A blend of SMA, EPM and amine-modified, high-molecular-weight EPDM (45/35/20; w/w/w) was prepared in the melt. The strand felt tough and transmission electron microscopy indicated a rubber dispersion with a micrometre morphology. The melt blend was extracted with THF to remove free SMA. The *FT*i.r. spectrum of the insoluble residue contained characteristic cyclic anhydride peaks at 1780 and 1860 cm^{-1} besides the expected EPM spectrum. Thus, SMA chains have been attached to the amine-containing EPDM. The reactivity of the modified EPDM towards SMA in the solution and melt blends agrees with the reac-
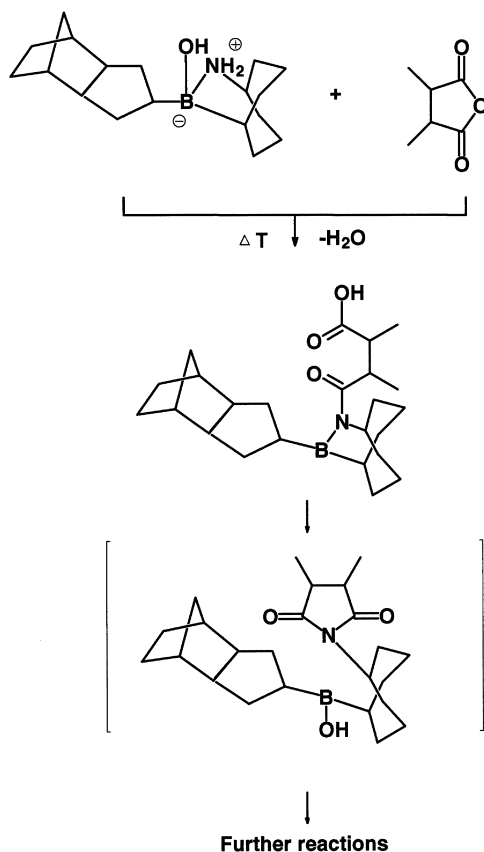
Fig. 5. Suggested mechanism for the reaction of the secondary-amine-containing EPDM or hydrogenated dicyclopentadiene with a cyclic anhydride as in phthalic anhydride or in poly(styrene-*co*-maleic anhydride).

tivity towards phthalic anhydride discussed above. It shows that although the structure of the modified EPDM is not the expected one with a primary amine, it does behave as one. The modified EPDM, therefore, seems to be a suitable *in situ* compatibilizer to be applied in SMA/EP(D)M blends.

It is not clear why the modified EPDM with its protonated secondary amine inserted in the attached 9-BBN unit reacts like a primary amine. In order to shed more light on this some model experiments were performed with the amine-containing DCPDH.

3.6. Modification of amine-containing DCPDH

*FT*i.r. showed that the amine-containing DCPDH/9-BBN adduct was stable when stored at 4°C for several months. As was already shown by the t.g.a., heating of the amine-containing DCPDH resulted in the loss of a molecule of water. Heating the amine-containing DCPDH at or above 150°C resulted in dramatic changes in the i.r. spectrum. Not only the characteristic peak at 1600 cm^{-1} and the peaks in the 3100–3400 cm^{-1} region disappeared, but in fact the whole i.r. fingerprint changed. G.c./m.s. showed that the main products are still the two amine-containing DCPDH isomers with the amine group inserted in the 9-BBN moiety ($m/e = 271$ g mol^{-1}). *FT*i.r. showed that storing the heated

residue in the laboratory resulted in the slow re-occurrence of the original modified DCPDH with the protonated secondary amine. This leads to the conclusion that heating the amine-containing DCPDH not only results in the reversible loss of a molecule of water, but also in the conversion of the original zwitterionic $RR'B^-(OH)NH_2^+R''$ into a neutral $RR'BNHR''$ structure.

Reacting amine-modified DCPDH with phthalic anhydride at room temperature showed the formation of an amide, as evidenced by the new i.r. peaks at 1540 and 1640 cm^{-1}. Probably, an amic acid is formed, which is the usual reaction product of a secondary amine and a cyclic anhydride. The carboxylic acid peak of the amide acid at 1710 cm^{-1} is almost absent, which may be due to hydrogen bond formation. *FT*i.r. showed that heating a mixture to 150°C resulted in a decrease in intensity of the two amide peaks and the occurrence of a strong imide signal at 1710 cm^{-1}. Heating at 250°C resulted in the disappearance of the amide peaks and the observation of a strong and a weak imide signal at 1710 and 1780 cm^{-1}, respectively. M.s. analysis of the heated residue did not allow identification of the products formed.

In summary, it is concluded that both amine-containing EPDM and DCPDH have a secondary amine inserted in the 9-BBN ring (Fig. 3), which at high temperature reacts with a cyclic anhydride as a primary amine towards an imide. Unfortunately, we have not been able to fully elucidate the new structures formed. Therefore, we can only make some suggestions with respect to the structures formed and their mechanism of formation (Fig. 5). As evidenced by i.r., first the amic acid is formed. The subsequent reaction is probably driven by the ring tension in the 9-BBN moiety with the inserted amine and the high stability of a cyclic imide relative to an amic acid. It is assumed that the B–N bond breaks, the amic acid converts into a cyclic imide and a B–OH structure is formed. The latter species obviously is an intermediate and finally a mixture of dimeric and oligomeric structures is formed, which will not be volatile and will be hard to characterize.

4. Conclusions

Hydroboration of EPDM with DCPD as diene monomer proceeded smoothly and all unsaturation was converted. Consequent amination resulted in the formation of an equivalent of amine. However, since the chemical structure of the amine-containing EPDM could not be elucidated in a straightforward fashion, a low-molecular-weight analogue of EPDM, namely DCPDH, was hydroborated and subsequently aminated. M.s., elemental analysis and ^{11}B n.m.r. showed that the amine-modified DCPDH still contained the elements of a 9-BBN residue in addition to the expected amine. X-ray diffraction showed the formation of a zwitterionic $RR'B^-(OH)NH_2^+R''$ species. Hence, a NH unit is inserted in one of the B–C bonds of the 9-BBN moiety of

the DCPDH/9-BBN adduct and not in the B−C bond connecting DCPDH with 9-BBN. Upon heating, a molecule of water is lost and the zwitterionic $RR'B^-(OH)NH_2^+R''$ species is converted to a neutral $RR'BNHR''$ species. Pyrolysis/g.c./m.s., e.s.c.a., elemental analysis and ^{11}B n.m.r. showed that the structure of the amine-modified EPDM is identical to that of the amine-containing DCPDH. In the presence of cyclic anhydrides, such as phthalic anhydride or SMA, the secondary amine of the amine-containing DCPDH and EPDM reacted as a primary amine, resulting in the formation of a cyclic imide at elevated temperatures. The aminated EPDM is shown to be an effective compatibilizer for SMA/polyolefin blends.

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