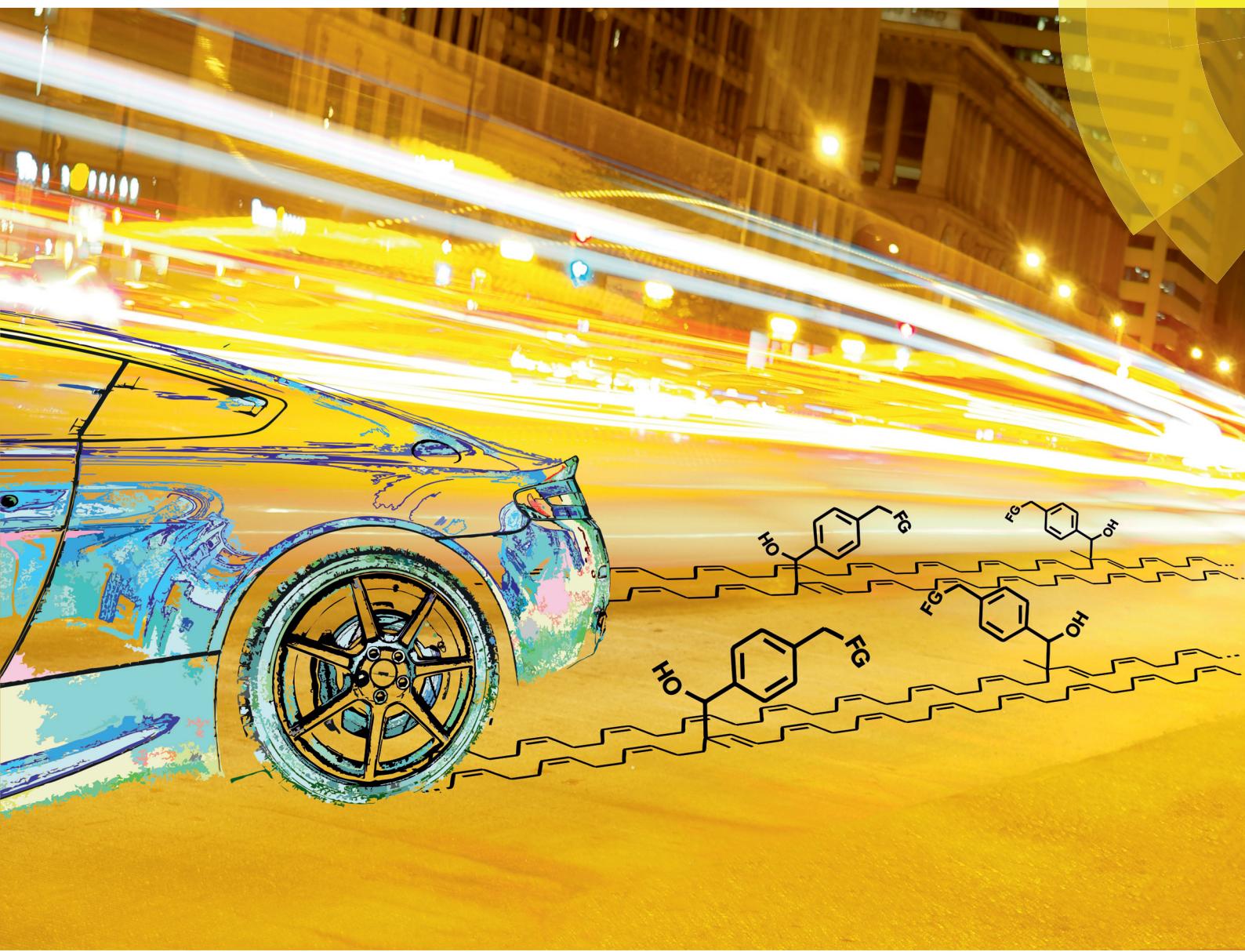


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Allylboration as a versatile tool for the *in situ* post-polymerization functionalization of 1,4-cis-poly(butadiene)

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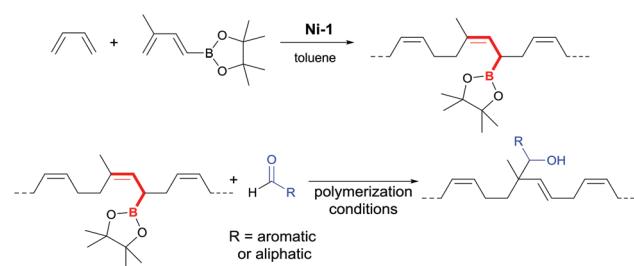
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Allylboration is a versatile tool for the post-polymerization functionalization of poly(butadiene-*co*-[4,4,5,5-tetramethyl-2-(3-methyl-1,3-butadienyl)-1,3,2-dioxaborolane]). Polar functionalized aldehydes $\text{HC(O)C}_6\text{H}_4(\text{CH}_2)\text{R}$ ($\text{R} = \text{Br, NR}_2, \text{PPh}_3, \text{P(O)(OEt)}_2$) react readily with the allyl boronic acid ester groups in the copolymer without interfering with the reactive double bonds in the polymer backbone. This provides access to stereoregular poly(butadiene) functionalized with a broad range of polar groups. Functionalization proceeds under polymerization conditions and therefore does not require a prior polymer work-up.

The synthesis of copolymers based on polar and nonpolar olefins *via* insertion polymerization is a challenging goal of polymer chemistry. Fundamental progress has been made recently in the polymerization of ethylene with polar vinyl monomers.^{1–4} The functionalization of poly(dienes) *via* direct copolymerization with polar monomers, however, is almost exclusively accomplished by free-radical or anionic methods.^{5–8} Polar functionalized poly(dienes) thus obtained can possess superior interactions with typical filler materials in tire applications such as silica or carbon black.^{9,10} However, the lack of microstructure control in these free-radical or anionic polymerizations is a major drawback because the properties of the poly(dienes), and hence their applicability, are strongly dependent on their polymer microstructure. Although progress has been made very recently towards copolymerizing 1,3-butadiene (BD) and isoprene (IP) with a broad variety of polar functionalized dienes to stereoregular copolymers, there are still functionalities that withdraw themselves from direct copolymerization.^{9,11} Post-polymerization functionalization is widely applied in poly(diene) chemistry. Vulcanization in the rubber industry is a prominent example. The reactivity of sulfur compounds with double bonds was also applied in the functionalization of 1,2-poly(butadiene) and poly(isoprene-*co*-

3-methylenehepta-1,6-diene) *via* the thiol-ene reaction.^{10,12–14} Although the functionalizations were successful, they still require additional activation, namely UV-irradiation and/or the addition of radical initiators. However, this approach cannot be utilized for high 1,4-*cis*-poly(butadiene) (PBD) as cross-linking occurs under the functionalization conditions.¹³ A mild method for a versatile post-polymerization functionalization of 1,4-*cis*-poly(butadiene) with a reactivity approach orthogonal to the backbone's double bonds is highly desirable.

For this purpose we explored the allylboration reaction of allyl boronic acid ester groups (Scheme 1) in poly(butadiene-*co*-[4,4,5,5-tetramethyl-2-(3-methyl-1,3-butadienyl)-1,3,2-dioxaborolane]) for post-polymerization reactions to introduce functional groups. High 1,4-*cis*-poly(butadiene-*co*-[4,4,5,5-tetramethyl-2-(3-methyl-1,3-butadienyl)-1,3,2-dioxaborolane]) was synthesized straightforwardly *via* direct insertion copolymerization of BD and 4,4,5,5-tetramethyl-2-(3-methyl-1,3-butadienyl)-1,3,2-dioxaborolane catalyzed by the cationic nickel complex $[(\text{allyl})\text{Ni}(\text{mesitylene})](\text{BAr}^{\text{F}}_4)$ Ni-1.¹¹ 4,4,5,5-Tetramethyl-2-(3-methyl-1,3-butadienyl)-1,3,2-dioxaborolane was chosen as a comonomer, because it is easily accessible through hydroboration of 2-methylbut-1-en-3-yne in excellent yields and high purity. Additionally, it readily generates the desired allyl boronic acid ester group in the polymer backbone upon insertion (Scheme 1).



Scheme 1 Formation of an allyl boronic acid ester group in the copolymer employed and conversion in an allylboration reaction.

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† Electronic supplementary information (ESI) available: Selected NMR-spectra and synthetic procedures. See DOI: 10.1039/c6py01388k



Initial experiments with an allylboronic acid pinacol ester as a small molecule model compound were designed to investigate the behavior of the reaction under conditions comparable to those of the desired application. All model reactions with the allylboronic acid pinacol ester and different aldehydes (pentanal, benzaldehyde, *p*-NO₂-benzaldehyde, *p*-dimethylaminobenzaldehyde, and 4-(1-pyrrolidinyl)benzaldehyde) showed the allylboration reaction to be a potentially robust and easy method for the introduction of functional groups into the backbone of poly(dienes). The expected products were formed in good (*e.g.* 73% with *p*-dimethylaminobenzaldehyde) to high yields (*e.g.* 89% with *p*-NO₂-benzaldehyde) as observed by means of ¹H NMR.

To assess the general reactivity of aldehydes towards the allyl boronic acid ester groups in the polymer backbone, 500 mg copolymer were reacted with 10 equiv. benzaldehyde (60 °C, 2–3 days in 5 mL toluene). The excess of benzaldehyde was removed subsequent to the reaction by precipitation of the polymer in methanol. After drying under reduced pressure, the polymer was characterized comprehensively by NMR spectroscopy.

The full conversion of the allylboronic acid pinacol ester groups in the copolymer to the desired secondary alcohol is evident by comparing key signals in the copolymer before and after the allylboration reaction (Fig. 1). While the signals for the vinylic CH₃ group 1, the olefinic proton 2, and the CH₃ groups of the pinacol ester 3 disappear, a set of new key resonances can be found in the product. These key resonances include the OH-substituted CH group 4 with a distinctive shift in ¹H (4.38 ppm) as well as ¹³C NMR (80.8 ppm). In addition, a signal for the newly formed biallylic CH₂ group 5 resonates at δ = 2.79 ppm (¹³C: 30.8 ppm), the peak of the CH₃ group 1 shifts from 1.69 ppm to 1.04 ppm, and the signals of the aromatic protons of the aryl ring 7 appear between 7.15 and 7.32 ppm. These observations and the chemical shift of the quaternary carbon atom 8 (44.5 ppm) prove the nucleophilic substitution to proceed highly selectively in an S_N2' fashion. Signals indicating the formation of the product formed in the

substitution following an S_N2 mechanism or other side-reactions were not observed.

To enlarge the scope of this functionalization approach, further different aldehydes were reacted with the copolymer: the full conversion of the allylboronic acid pinacol ester groups of the copolymer with pentanal under otherwise identical conditions showed that the reactivity is not limited to aromatic aldehydes and also that alkyl aldehydes are suitable reagents for functionalization of diene copolymers *via* an allylboration reaction. Quantitative conversions are also observed when commercially available, N-functionalized, aromatic aldehydes are used. Both, 4-(1-pyrrolidinyl)benzaldehyde and *p*-dimethylaminobenzaldehyde were individually reacted for two days with the copolymer under otherwise identical conditions as the reaction with benzaldehyde. NMR analyses after repeated precipitation of the polymers showed in both cases additional signals compared to the polymer functionalized with benzaldehyde: The polymer functionalized with 4-(1-pyrrolidinyl)benzaldehyde exhibits both ¹H and ¹³C signals for the pyrrolidine moiety at δ = 3.28 ppm (47.7 ppm) and 2.00 ppm (25.6 ppm). In the case of *p*-dimethylaminobenzaldehyde, both methyl groups resonate at 2.94 ppm as a key signal in the proton NMR spectrum.

The aforementioned studies were all conducted with a separately synthesized copolymer. However, functionalization is desirable without an additional step (*i.e.* work-up of the polymer) directly after the copolymerization of butadiene with 4,4,5,5-tetramethyl-2-(3-methyl-1,3-butadienyl)-1,3,2-dioxaborolane. For this purpose, we ran two copolymerizations under standard polymerization conditions.¹⁵ At the end of both polymerizations, benzaldehyde (42 equiv. to comonomer) or 4-(1-pyrrolidinyl)benzaldehyde (10 equiv. to comonomer) was added. Both reaction mixtures were then stirred at 50 °C and the conversion was followed by ¹H NMR taking aliquots. The reaction with benzaldehyde showed a degree of functionalization of *ca.* 50% after 48 min and complete functionalization after two hours. The reaction using 4-(1-pyrrolidinyl)benzaldehyde, however, proceeded significantly

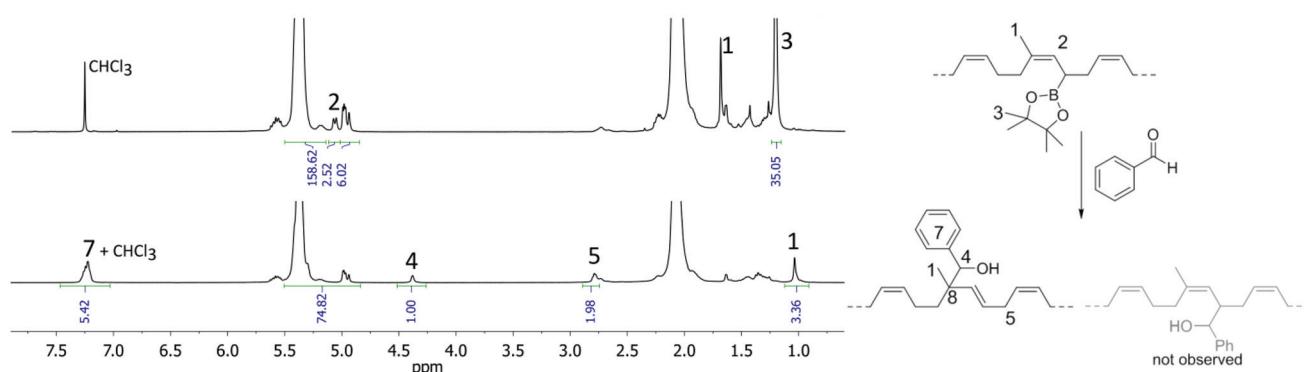


Fig. 1 ¹H NMR spectra of the copolymer before and after the allylboration reaction with benzaldehyde showing the selective formation of the product structure expected for an S_N2' substitution mechanism.



slower. After 2.5 h only 25% of the allylboronic acid ester groups in the copolymer were converted. A conversion of 50% was reached after 28 h and full functionalization was reached after two days. This difference in the reaction rates is possibly due to the different amounts of aldehyde compared to that of the comonomer, or due to a deactivating influence of the amine group on the *para*-position to the aldehyde moiety.

This outcome prompted us to engage in the synthesis of aromatic aldehydes with a methylene group as a spacer between the aromatic ring and the functional group.

Additionally, this approach should generate a platform to synthesize aromatic aldehydes with different functional groups.

Syntheses of differently functionalized aromatic aldehydes were accomplished *via* two different routes (Scheme 2). Route (A) encompasses the functionalization of 1-bromo-4-(bromomethyl)benzene with a nucleophile (*e.g.* pyrrolidine) followed by conversion to the desired aromatic aldehyde by reaction with *n*-BuLi and DMF followed by an acidic aqueous work-up. Both steps give the desired product in high yields and purity, making purification steps like distillation or column chromatography unnecessary. However, not all functional groups that can be introduced this way are stable towards the conditions in the second step. Therefore, we also used a second route to synthesize functionalized aromatic aldehydes. Route (B) starts with the synthesis of 4-(bromomethyl)benzaldehyde which can be directly reacted with a nucleophile (*e.g.* PPh_3). If the nucleophile is reactive towards the aldehyde group (*e.g.* NaP(O)(OEt)_2), the application of well-known protecting group chemistry enables the successful synthesis of the desired product. Except for the first step, the synthesis of 4-(bromomethyl)benzaldehyde, no further purification was necessary for the obtained products.

To gain more information about the reaction's actual progress over time influenced by the *para*-substituents, we followed the reaction of the copolymer with benzaldehyde, 4-(1-pyrrolidinyl)benzaldehyde, and 4-(pyrrolidinylmethyl)benzaldehyde by ^1H NMR (12 equiv. of aldehyde to comono-

Table 1 Different aldehydes used in the allylboration reaction, showing the influences of substitution pattern and equivalents used (compared to functional groups present in the copolymer)

Entry	Aldehyde	Equiv. ^a	Conversion of the polymers' functn. groups (time) ^b
1		12	99% (75 min)
2		12	38% (235 min) 99% (21 h)
3		12 1	99% (95 min) 99% (18.5 h)
4		1	99% (18.75 h)
5		1	99% (20.3 h)
6		0.7 +0.5 ^c	70% (22.5 h) 99% (+2.3 h)

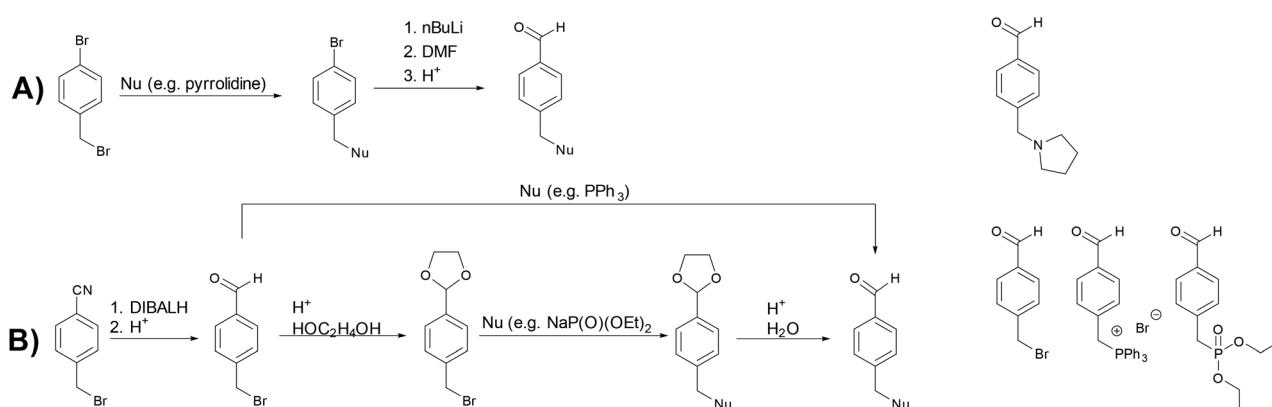
Reaction conditions: 65 mg polymer, 0.6 mL CDCl_3 , 60 °C.

^a Equivalents of aldehyde compared to functional groups present in the polymer. ^b Conversion of the functional groups in the polymer, determined from ^1H NMR spectra. ^c Additional 0.5 equiv. of aldehyde were added after 22.5 h, full conversion was observed after additional 2.3 h.

mer units, 60 °C, Table 1 entries 1–3). The reactivity differences of the compared aldehydes are significant: The conversion with benzaldehyde reached 60% after 10 min and full conversion after 75 min (Table 1, entry 1). In comparison, the reaction with 4-(1-pyrrolidinyl)benzaldehyde is much slower as 38% conversion is reached after 235 min and full conversion requires heating overnight (Table 1, entry 2).

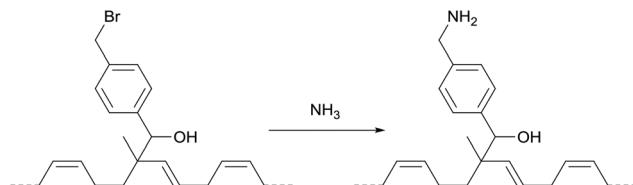
The reaction with 4-(pyrrolidinylmethyl)benzaldehyde is again significantly faster and proceeds with rates comparable to those observed for the allylboration reaction using benzaldehyde (full conversion after 95 min, Table 1, entry 3).

The high reactivities of the synthesized functionalized aromatic aldehydes and the clean and selective formation of the



Scheme 2 Syntheses of differently substituted aromatic aldehydes with a CH_2 -linker.





Scheme 3 Generation of -NH₂ groups by reaction of a product of allyl-boration with ammonia.

desired target structure allows the use of equimolar or even substoichiometric amounts of aldehyde (Table 1, entries 3–6). Although longer reaction times are required for equimolar reactions, a waste of reagents is avoided. Allylboration reactions with all synthesized aromatic aldehydes were successfully performed and the obtained functionalized polymers were scrutinized by NMR-spectroscopy to prove the complete functionalization of 1,4-*cis*-poly(butadiene) (for NMR spectra and assignments *cf.* the ESI†).

The polymer obtained with 4-(bromomethyl)benzaldehyde (entry 4) can be functionalized further by virtue of the electrophilic nature of the bromobenzyl-moiety. Notably, this allowed the introduction of primary amine groups by reaction with ammonia (Scheme 3; for details see the ESI†).

In conclusion, we have shown that the allylboration reaction is a versatile and robust tool for the post-polymerization functionalization of 1,4-*cis*-poly(butadiene). Allyl boronic acid ester groups in poly(butadiene-*co*-[4,4,5,5-tetramethyl-2-(3-methyl-1,3-butadienyl)-1,3,2-dioxaborolane]) react readily with *para*-functionalized aromatic aldehydes to give access to functionalized high 1,4-*cis*-poly(butadienes) that are not accessible *via* a direct copolymerization approach. The allylboration reaction can be performed directly after polymerization without the need for a prior work-up of the polymer and proceeds quantitatively in an S_N2' fashion without the occurrence of side-reactions.

Acknowledgements

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- 15 20 µmol **Ni-1**, 20 mL toluene, 1.05 bar BD, 0.7–0.8 mmol comonomer, 25 °C, 30 min.

