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Cyclopropanation of poly(isoprene) using NHC-Cu (I) catalysts: Introducing carboxylates

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Abstract

The incorporation of functional groups into unsaturated polyolefine-polymers often represent a challenging task. Based on the known cyclopropanation of double bonds with diazoesters in the presence of metal-catalysts of low molecular weight compounds, we in this article develop an approach to decorate the polymer backbone of poly(diene)s with ester as well as carboxylic groups via cyclopropanation. Therefore, predominantly *cis*-1,4-poly(isoprene)s are converted with ethyl or *tert*-butyl diazoacetate using copper(I) *N*-heterocyclic carbene (NHC) catalysts, while focusing on the technically relevant cyclohexane as solvent. The application of commercially available NHC-Cu(I) catalysts results in modification degrees of 4–5%, while an increased solvent polarity, like dichloromethane, results in up to 17% modification. The resulting esters were further converted to the corresponding free carboxylic groups by deprotection using trifluoroacetic acid. Thus, an introduction of functional groups along the polymer backbone with a wide variety of application, like ionic interaction or hydrogen bonding motifs, was successfully demonstrated. Its potential for upscaling makes this approach feasible for an application in large-scale production processes, such as for manufacturing of modified synthetic rubbers.

KEYWORDS

copper(I) catalyst, cyclopropanation, diazoacetate, *N*-heterocyclic carbene, poly(diene)

1 | INTRODUCTION

The chemical transformation of double bonds to cyclopropanes is conventionally accomplished by application of highly reactive species, such as carbenes, ylides and carbanions, or the assistance of metal catalysts.[1–2] A prominent example is the metal-catalyzed cyclopropanation,[3] which is known as a powerful tool to introduce different functional groups to small molecules as well as into the scaffold of poly(diene)s, thus enabling a broad variation of material properties.

A number of methods for cyclopropanation reactions were reported, like the classic Simmons-Smith-protocol, which uses the methylene iodide and zinc–copper couple to modify low molecular weight alkenes, such as 1-octene, in yields up to a 70%.[4–6] Furthermore, allylic

alcohols or poly(butadiene)s were modified by carbene addition, where the required free carbenes were generated under alkaline conditions *via* decomposition of halomethanes[7] like chloroform or bromoform.[8–9] However, in many cases a significant degradation of the polymer backbone has then to be considered yielding polymers with significantly lower molecular weights.[7] Cyclopropanation of unsaturated moieties by generating carbenoids using diazo compounds in the presence of transition metal-catalysts is a particularly versatile method reported in the literature, even if usually applied only for low molecular weight olefins.[10] Frequently used metal-catalysts based on palladium and rhodium,[11–14] but also Cu(I/II)-based catalysts were considered for such cyclopropanations.[15–18]

Cyclopropanation of poly(diene)s, like poly(isoprene) (PI) or poly(butandiene), are only rarely known examples in the literature. Thus for instance a cyclopropanation of predominantly 1,2-*syn*-polybutadiene (1,2 linkage ∼70 mol%) has been reported with methyl diazoacetate and a copper(I) triflate benzene complex ([Cu OTf]·0.5C$_6$H$_6$) as catalyst, achieving up to 33 mol% cyclopropane modification corresponding to the polymer double bonds in dichloromethane (DCM),[3] albeit no preference to 1,2- or 1,4-linkages could be observed.[3] A more sophisticated approach used a [Tp^{Br3}Cu(NCMe)] catalyst (Tp^{Br3} = hydrotris[3,4,5-tribromo-1-pyrazolyl]borate) in the presence of ethyl diazoacetate (EDA) to modify 1,2- and 1,4-*cis*-polybutadiene revealing 80% up to 100% functionalization of the corresponding double bonds.[19] However, the synthesis of the catalyst [Tp^{Br3}Cu(NCMe)][20] proceeds *via* the highly toxic Tl[Tp^{Br3}] thallium

precursor.[21] Though the obtained results are remarkable, the scale-up of the catalyst production is highly restrictive due to the toxicity of the thallium. Hence, it became of interest to find alternative metal catalysts that could achieve a cyclopropanation with diazo esters. Therefore, catalytic systems based on *N*-heterocyclic carbene (NHC) ligand–metal complexes has caught our attention due to the minimal ligand dissociation related to the strong interactions between the NHC-ligand and the metal center.[22] Metal-mediated cyclopropanation of unsaturated low molecular weight compounds with diazoacetates using Pd(0),[23] Au(I),[24–25] and Cu(I)[26–27] have been reported. However, to the best of our knowledge, all those catalysts were applied only for low molecular weight compounds and not yet for polymers.

We here report on cyclopropanations of PI using NHC-Cu(I) catalysts, enabling an easy access to modified poly(diene)s bearing ester- or carboxylic-acid-groups. The modified PI should be able to establish ionic interactions with cations or cationically modified polymers or establish hydrogen bonds to form dynamic networks and offer thus the opportunity to be applied in the tire/rubber industry, increasing durability and grip. In a first step, predominantly *cis*-1,4-PIs were reacted in the presence of commercially available Cu(I)-NHC catalysts with ethyl- as well as *tert*-butyl diazoacetates (*t*-BDA) to generate ester-substituted cyclopropane along the PI backbone (See Scheme 1). Copper was selected as the transition metal, as it is less toxic than thallium and less expensive compared to palladium or gold. Moreover, Cu-mediated cyclopropanations are known to be conducted under mild reaction conditions.[10] To the best of our knowledge, no reports are published using
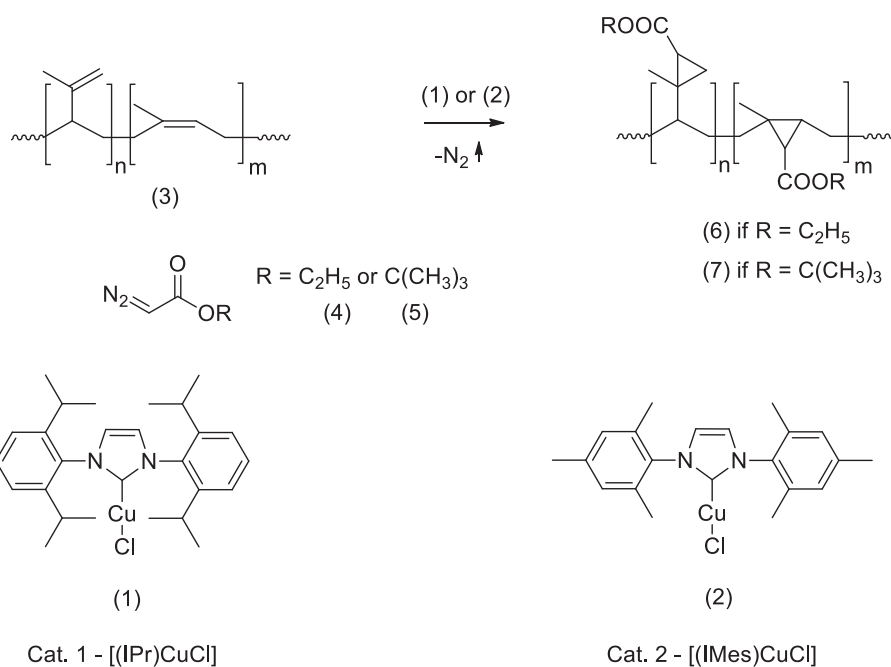
SCHEME 1 Metal-catalyzed cyclopropanation of a predominantly *cis*-1,4-poly(isoprene) with the NHC-Cu(I)-based catalyst (1, 2) and the diazoacetates (4, 5). NHC, *N*-heterocyclic carbene

NHC-Cu(I) catalyzed cyclopropanation of poly(diene)s *via* diazoacetates, thus presenting the use of NHC-Cu(I) complexes as an alternative to previously mentioned toxic or expensive transition metals.[19]

2 | EXPERIMENTAL SECTION

2.1 | Materials

EDA (87 wt% in DCM) (**4**), *t*-BDA(85 wt% in DCM) (**5**), chloro[1,3-bis(2,6-diisopropylphenyl) imidazol-2-ylidene] copper(I) (Cat. **1**), 1,2-dichloroethane (1,2-DCE, 99.8%), and trifluoroacetic acid (TFA, 99%) (**8**) were purchased from Sigma–Aldrich, while chloro[1,3-bis(2,4,6-trimethylphenyl) imidazol-2-ylidene]copper(I) (Cat. **2**; 97%) was purchased from TCI. PI ($M_{n,GPC,corr}$ = 2,900 g/mol) (90:8 = 1,4-PI: 3,4-PI; 65:25 = 1,4-*cis*: 1,4-*trans*) (**3**) was provided by Trinseo. All were used as received. Cyclohexane (99. 5%; Grüssing) was dried in the presence of sodium for the reaction.

2.2 | Methods

Nuclear magnetic resonance (NMR) spectra were measured on a Gemini 2000 FT-NMR (400 MHz) spectrometer by Varian and deuterated solvents were used for the measurements. The chemical shifts are given in parts per million (ppm) and referred to the remaining solvent signals of CDCl$_3$ at 7.26 ppm and DCM-d_2 at 5.34 ppm. The obtained spectra were analyzed using MestReNova (9.0).

Analytic GPC was performed on a Viscotek GPCmax VE 2002 using a column set of a H$_{HR}$H Guard-CLM3008 and a GMH$_{HR}$-N-18055 main column in tetrahydrofuran (THF) with a flow rate of 1 ml/min and a column temperature of 22°C. Detection was accomplished by refractive index with a VE 3580 RI detector of Viscotek at 35°C. External calibration was done using PS standards with a molecular weight range from 1,050 to 115,000 g/mol were used.

Attenuated total reflection-infrared (ATR-FTIR) measurements were done on a Bruker Tensor VERTEX 70 spectrometer equipped with a Golden Gate Heated Diamond ATR Top-plate. Opus 6.5 was used for data analyzing.

Differential scanning calorimetry (DSC) was performed on a differential scanning calorimeter 204F1/ASC Phoenix from Netzsch (Selb, Germany). Crucibles and lids made of aluminum were used. Measurements were performed in a temperature range of −100–100°C from using heating 10 K/min. As purge gas, a flow of dry argon was used. For evaluation of data, the Proteus Thermal Analysis Software (Version 5.2.1, NETZSCH-Geraetebau GmbH, Selb, Germany, 2011).

Rheology was performed on an oscillatory plate rheometer MCR 301/SN 80753612 from Anton Paar (Graz, Austria). All measurements were performed using a PP08 measuring system (parallel plated, diameter 8 mm). Oscillatory frequency sweep was conducted with 5% strain and frequency range from 100 to 0.1 Hz with a decadal logarithmic ramp of 5 pt/dec.

2.3 | Cu(I)-catalyzed cyclopropanation of PI (1) with diazoacetates (4, 5)

All reactions were carried out under inert conditions using common Schlenk techniques and all solvents were degassed freshly by at least three freeze-pump-thaw cycles prior use. PI (6 g; corresponding to 88.0 mmol functional groups; $M_{n,GPC,corr}$ = 2,900 g mol^{-1}, DP = 42) was dissolved in dry solvents (1,2-DCE, cyclohexane, DCM or THF). The copper(I) catalysts (**Cat. 1/2**) (0.05 eq. per double bond [DB], 4.5 mmol) were added as a solution. If the reaction solvent was cyclohexane, the catalysts were added in DCM (minimum volume required to solubilize the catalyst) which was later removed by vacuum. Subsequently, the diazoacetate (DA) (EDA (**4**)/ *t*-BDA (**5**), 2 eq. per DB, 180 mmol) was added as diluted solution in the appropriate solvent (1,2-DCE, DCM, THF or cyclohexane) by a dropping funnel over a period of 4 hr. A water bath at rt was used to keep the exothermicity in check. The final total volume of the solvents was based on the concentrations of 1.3, 10, 15, or 20 wt% of PI, as desired. The reaction was stirred for 48 hr at room temperature. Unless the reaction was conducted in cyclohexane, the solvent was removed under vacuum and the contents of the flask were resolubilized in cyclohexane. The crude product was purified by precipitating thrice in cold methanol (−50°C), collected, and dried in high vacuum giving (**6/7**) in 60–65% yields.

For EDA-modified PI (**6**) = PDI = 1.1, ^{1}H-NMR (400 MHz, CDCl$_3$) δ 5.10 (dt, J = 15.0, 6.4 Hz, 29H), 4.80–4.63 (m, 7H), 4.09 (dqt, J = 9.7, 7.2, 3.1 Hz, 17H), 2.03 (q, J = 15.7, 12.3 Hz, 110H), 1.67 (d, J = 7.6 Hz, 69H), 1.58 (s, 15H), 1.28–1.18 (m, 32H), 0.88 (t, J = 6.6 Hz, 3H).

For *t*-BDA-modified PI (**7**) = $M_{n,GPC,corr}$ = 3,200 g mol^{-1}, PDI = 1.1, ^{1}H-NMR (400 MHz, CDCl$_3$) δ 5.11 (dt, J = 14.9, 6.4 Hz, 37H), 4.79–4.63 (m, 8H), 2.12–1.94 (m, 151H), 1.68 (s, 74H), 1.64 (d, J = 11.8 Hz, 13H), 1.44 (s, 17H), 0.88 (t, J = 6.7 Hz, 3H). ATR-FTIR: ν (cm^{-1}) = 2,960 (s), 2,925 (s), 2,853 (s), 1720 (m, $ν_{CO}$), 1,645 (w), 1,445 (s), 1,375 (s), 1,145 (s), 1,085 (w), 858 (m), 836 (m), 672 (m), 625 (s), 534 (s), 464 (s).

2.4 | Cu(I)-catalyzed decomposition of EDA (4)

All reactions were carried out in a glovebox and the DCM-d_2 was opened and used as obtained inside the glovebox. The copper(I) catalyst (**Cat. 1** = 10.8 mg/**Cat. 2** = 9 mg) (1 eq.) was added to a glass vial and dissolved in DCM-d_2 (0.2 ml). Subsequently, the EDA (**4**) (40 eq.) was added dropwise. The reaction was stirred for 24 hr at room temperature after which samples were collected and sent for NMR.

For Cat. 1-^{1}H-NMR (400 MHz, DCM-d_2) δ 6.82 (s, 1H$_{trans}$), 6.23 (s, 1H$_{cis}$), 4.22 (dq, J = 9.7, 7.1 Hz, 4H), 1.36–1.16 (m, 6H).

For Cat. 2-^{1}H-NMR (400 MHz, DCM-d_2) δ 6.81 (s, 1H$_{trans}$), 6.23 (s, 1H$_{cis}$), 4.22 (dq, J = 9.8, 7.1 Hz, 4H), 1.36–1.14 (m, 6H).

2.5 | Deprotection of cyclopropanated PI (9*)

The deprotection of (**7***) (0.2 g; 0.0625 mmol; $M_{n,GPC,corr}$ = 3,200 g/mol, DP = 42; corresponding to 3 mmol functional groups) was accomplished treating a solution of (**7***) in DCM (5 ml) with TFA (**8**) (30 mmol) under vigorous stirring for 24 hr. The solvent and remaining TFA were removed under vacuum. The crude product was dissolved in cyclohexane and precipitated into cold methanol (−50°C) for at least three times. The final product (**9***) was obtained after drying in high vacuum.

ATR-FTIR: ν (cm^{-1}) = 3,370 (w, ν_{OH}), 2,925 (s), 2,865 (s), 1778 (m), 1700 (m, ν_{CO}), 1,455 (m), 1,375 (m), 1,217 (m), 1,167 (m), 1,026 (m).

3 | RESULTS AND DISCUSSIONS

3.1 | Cu(I)-catalyzed cyclopropanation of PI with diazoacetates

In a first set of experiments, the catalytic cyclopropanations of predominantly *cis*-1,4-PIs (90:8 = 1,4-PI: 3,4-PI; 65:25 = 1,4-*cis*: 1,4-*trans*) (PI) (**3**) were conducted using EDA (**4**) in the presence of two different Cu(I)-NHC catalysts, Cat. **1** [(IPr)CuCl] and Cat. **2** [(IMes)CuCl] (see Scheme 1). The ratio of EDA per PI DB was set to 1:2 and the solvent was fixed to cyclohexane with a PI concentration of 1.3 wt%. The reaction conditions were subsequently optimized in in view of the catalyst amount and the reaction temperature (see Table 1). The ratio of the catalyst was varied from 0.002 to 0.05 eq. per DB of PI, where 0.05 eq. was determined as best with modifications of 3% (Cat. **1**) and 2% (Cat. **2**), respectively, (determined *via* ^{1}H NMR spectroscopy, for details see Appendix S1). Investigating the influence of the reaction temperature from room temperature to 40°C revealed no significant effect towards the modification yield, which remained around 3% for both catalysts (for details see Table 1). Hence, the reaction temperature was kept constant at room temperature.

In the next set of experiments, the influence of solvent polarities on the modification yield was investigated (Table 2). Therefore, the cyclopropanation was performed in THF, DCM, and cyclohexane (see Figure 1a). The use of cyclohexane as a solvent is of special interest as usually nonpolar solvents are used in industrial PI synthesis *via* living anionic polymerization. The best modification of 10% was obtained with Cat. **2** in DCM (see Table 2, **6a.i**), while THF and cyclohexane revealed only low PI

TABLE 1 Variations in catalyst amounts as well as a change of temperature to ascertain suitable reaction conditions

Entry no.	Ratio (cat.:PI:EDA)	Catalyst	T, °C	Percentage modification[a]
1	0.002:1:2	Cat. **1**	RT	0.5
2		Cat. **2**		0.4
3	0.02:1:2	Cat. **1**	RT	3.0
4		Cat. **2**		2.0
5	0.05:1:2	Cat. **1**	RT	3.0
6		Cat. **2**		2.0
7	0.05:1:2	Cat. **1**	40°C	3.0
8		Cat. **2**		3.0

Note: The reactions were performed in cyclohexane with the solid content (wt%) of PI in cyclohexane set at 1.3%. Reactions performed for 48 hrs..

Abbreviations: EDA, ethyl diazoacetate; PI, poly(isoprene).

[a]Calculated according to the ratio of the signals at the peaks at 5.10 ppm and 4.80–4.63 ppm belonging to 1,4- and 3,4-poly(isoprene), respectively, as well as the new peak after modification at 4.10 ppm belonging to the methylene protons of the —CO$_2$$CH_2CH_3$ moiety of the cyclopropane appearing in ^{1}H-NMR spectroscopy.

TABLE 2 Calculated percentage modification for cyclopropanated 1,4-PI with varying investigations

Entry no.		Investigations	Solvent	Solid content (wt%)	Percentage modification[a]	
					Cat. 1	Cat. 2
1		Virgin PI (3)	—		—	—
6a	i	Solvent variation	DCM	1.3	3	10
6a	ii		THF		2	2.5
6a	iii		Cyclohexane		3	2
6b	i	Solid content (wt%) variation	Cyclohexane	1.3	3	2
6b	ii		Cyclohexane	10	1.5	3
6b	iii		Cyclohexane	15	1.5	5
6b	iv		Cyclohexane	20	2.5	5
6c	i		DCM	15	—	17
6d	i	Cyclopropanation with *t*-BDA	DCM	10	2	4
6d	ii			15	—	5
6e		Cyclopropanation with EDA (**4**) in 1,2-DCE	1,2-DCE	15	5	4

Note: The ratio of the catalyst to per double bond of the PI to diazoacetate is set at 0.02:1:2 for **Entry 6a** and 0.05:1:2 for all other experiments. The Polydispersity Index (PDI) of all above listed experiments vary from 1.1 to 1.2 and the ratio of 1,4-/3,4-PI isomers remains approximately 9.

Abbreviations: DCE, 1,2-dichloroethane; DCM, dichloromethane; EDA, ethyl diazoacetate; PI, poly(isoprene); *t*-BDA, *tert*-butyl diazoacetate; THF, tetrahydrofuran.

[a]Calculated according to the ratio of the signals at the peaks at 5.10 ppm and 4.80–4.63 ppm belonging to 1,4- and 3,4-poly(isoprene), respectively, as well as the new peak after modification at 4.10 ppm belonging to the methylene protons of the —CO$_2$$CH_2CH_3$ moiety of the cyclopropane appearing in ^{1}H-NMR spectroscopy.
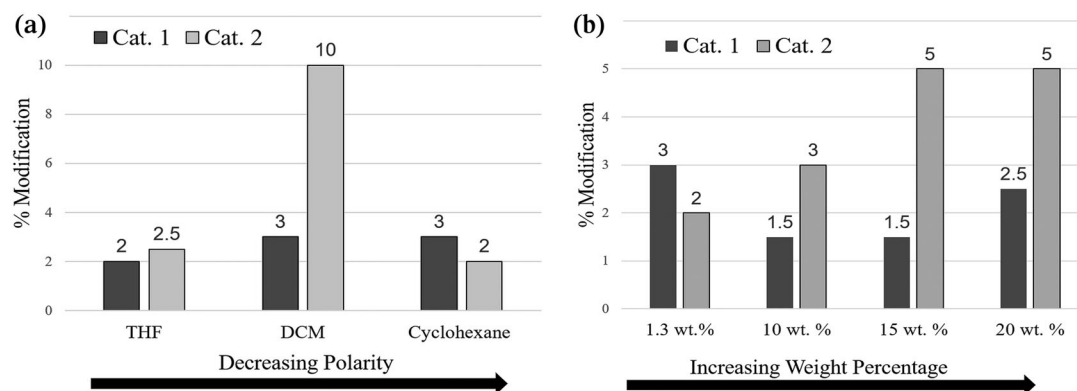

FIGURE 1 Dependency of cyclopropanation from PI with EDA and Cu(I)-NHC catalysis from (a) the solvent polarity at 1.3 wt% solid content and (b) the concentration in cyclohexane. EDA, ethyl diazoacetate; NHC, *N*-heterocyclic carbene; PI, poly(isoprene)

modification (2–3%) (see Table 2, **6a.ii** and **6a.iii**). The limited solubility of the catalysts in cyclohexane lead naturally to lower reaction rates and thus to a lower overall conversion.[28] Albeit the solubility in THF is good, its strong coordination to the copper caused a strong shielding of the catalytic active center, resulting finally in lower yields. Weakly coordinating polar solvents, such as DCM, are preferred for cyclopropanation reactions *via* carbenes to avoid significant solvent effects.[29] Hence, further reactions were conducted with DCM as the most

suitable solvent as well as with cyclohexane because of its industrial relevance.

To further optimize the reaction conditions, the PI solid content (wt% in solvent) was varied (see Table 2) from 1.3 to 20 wt% to increase the effective concentration of the reactive compounds, PI as well as EDA, expecting higher reaction rates and thus finally higher modification efficiencies. Accordingly, the modification yields increased in case of Cat. **2** from 2% for 1.3 wt% up to 5% for 15 wt% in cyclohexane (Table 2, **Entries 6b.i**

and 6b.iii, see Figure 1b). A further increase to 20 wt% showed no additional improvement. In comparison, the reaction conducted with 15 wt% solid content in DCM showed a superior modification with 17% (see Table 2, **Entry 6c.i**). However, for the higher concentrated solutions (15–20 PI wt%, see Table 2), a violent bubbling was observed, which was on the one hand the result of the faster reaction and thus stronger heat development due to the exothermic nature of the reaction, and on the other hand a result of the faster release of a larger amount of evolved N_2 gas generated in the course of the reaction. Hence, a slow, dropwise addition of the diazoacetates was necessary to avoid an uncontrolled explosion which occurred at higher concentrations than 20 wt%, limiting thus the test range.

Acknowledging that the initial experiments conducted with Cat:PI:EDA per double bond ratio of 0.02:1:2 had the highest modification degree of 10%, obtained with DCM with a solid content of 1.3 wt% (see Table 2, **Entry 6a.i**) with Cat. **2**, a variation of 15 wt% solid content of PI was also conducted in DCM (see Figure 2) with a ratio of 0.05:1:2. An effort was also made with another chlorinated solvent, 1,2-DCE, to observe the possible percentage modification (see Table 2, **Entry 6e**). However, DCM with a solid content of 15 wt%, had the highest modification of up to 17%, achievable with Cat. **2** (see Table 2, **Entry 6c.i**), compared to a modification of 4–5% achieved with both, 1,2-DCE and cyclohexane with a comparable solid content.
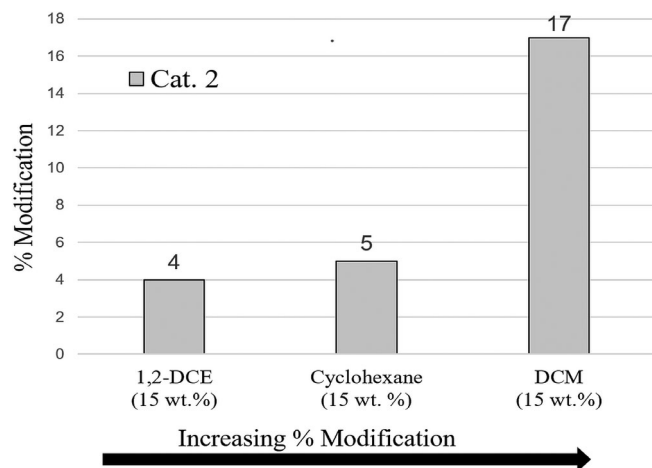

FIGURE 2 Comparison of the percentage modification with the variation of the solid content (wt%) in chlorinated solvents, 1,2-DCE and DCM compared to cyclohexane. The Cat:PI:EDA per double bond ratio is 0.05:1:2 and the percentage modification was determined by ^{1}H-NMR spectroscopy. DCE, 1,2-dichloroethane; DCM, dichloromethane; EDA, ethyl diazoacetate; NMR, nuclear magnetic resonance; PI, poly(isoprene)

Kinetic studies of the cyclopropanation of PI with EDA (**4**) were performed in cyclohexane at 20 wt% (as technical relevant conditions) to investigate differences in the reactivity of Cat. **1** and Cat. **2** (Table S1). The reaction was monitored *via* ^{1}H-NMR spectroscopy revealing the maximum conversion after 24 hr for Cat. **2** to 4% and 48 hrs for Cat. **1** to 1.5% (see Appendix S1, Figure S2). In order to understand the difference in modification yields by the two catalysts, it is important to consider the mechanistical pathways of the Cu(I)-catalyzed cyclopropanation reactions.[30–31] After an initial formation of a precatalyst due to the affinity of the active Cu(I) catalyst for the unsaturated substrate[15,29–30,32–34] (see Scheme 2, **III**), the cyclopropanation proceeds further *via* complexation of a metal and a carbene (**VI**), formed by expelling N_2 from the diazo compound (**V → VI**), which is considered as the rate determining step.[15] The ring closing step itself is known to proceed either *via* a one-step concerted pathway (**VII**) as a direct-carbene insertion, or *via* a two-step process, proceeding by a metallocyclobutane intermediate (**VIII**),[29,32,35] depending on the diazo compound, the ligand (L_n) and the transition metal (M).

Considering these theoretical assumptions, a possible explanation of the different reactivity of both catalysts can be found in the different donor properties of the NHC ligands. The pKa values are reported as 21.1 for Cat. **1** and 20.8 for Cat. **2**, respectively.[36] Even though the difference in the values is minimal, the pKa value of Cat. **1** could indicate to a higher electron density on the copper instead of the carbenic carbon in the case of Cat. **2**. Hence, Cat. **2** would act as a more efficient catalyst as the strength of backdonation from the Cu(I) to the incoming DA to form (**VI**) (see Scheme 2) would be higher, in consequence enhancing its reactivity. The steric effects of the catalyst could possibly have more influence on the reactivity of a catalyst. The percent buried volume ($\%V_{bur}$) is reported as 47.6% for Cat. **1** and 36.3% for Cat. **2**, respectively, for M-NHC length at 2.00 Å,[37] showing that Cat. **1** is bulkier compared to Cat. **2**. Therefore, the bulkier Cat. **1** could affect the mechanism, as suggested in Scheme 2, in two ways; by affecting the coordination of the diazoesters to the catalysts as suggested in (**VI**), as well as hindering the cyclopropanation itself, indicated by step (**VII/VIII**), making Cat. **2** a more effective and efficient catalyst.

However, we wonder why the overall modification yield was stuck at a relative low level. A feasible explanation was found in a potential premature decomposition of the diazo compound. Although previous literature has reported no decomposition of the EDA (**4**) in the presence of the [(IPr)CuCl] (Cat. **1**) until an unsaturated substrate was added,[26] we were able to determine a dimerization *via* ^{1}H-NMR spectroscopy (see
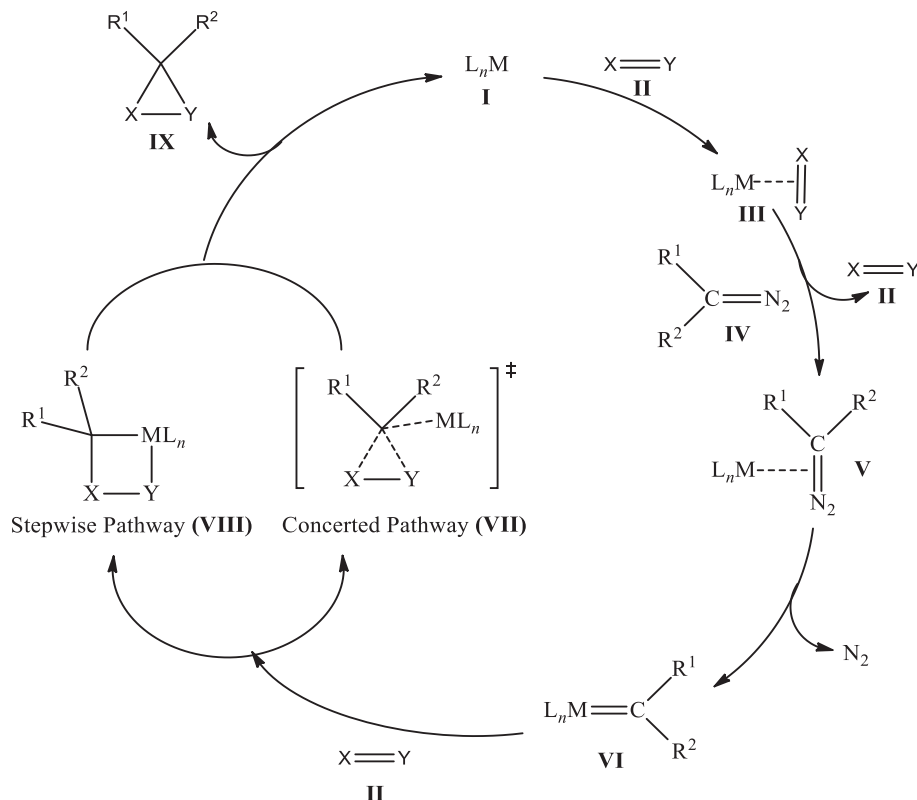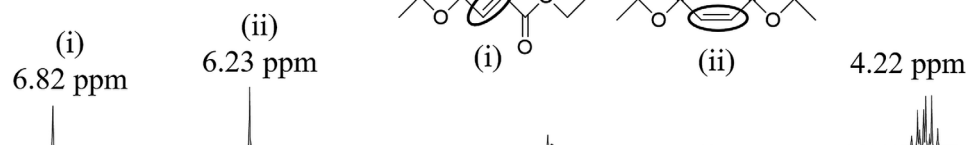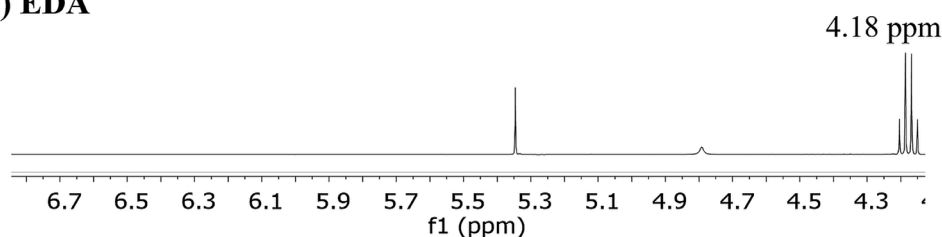
SCHEME 2 Mechanism of the metal-catalyzed cyclopropanation of olefins with diazo compounds.[16,29–30,32]

FIGURE 3 NMR spectra for EDA in the presence of (a) Catalyst **1** and (b) Catalyst **2**. The spectrum (c) is of EDA without a catalyst. All NMR are measured in the solvent DCM-d$_2$. DCM, dichloromethane; EDA, ethyl diazoacetate; NMR, nuclear magnetic resonance

Figure 3). In the presence of catalyst **1** or **2**, the EDA (**4**) (ratio of 40:1 to catalyst) underwent dimerization to form diethyl maleate and fumarate (solvent DCM-d$_2$), also in the absence of an unsaturated substrate, similar to other Cu(I) catalysts.[38] To study if the presence of PI mitigates this dimerization, further in situ NMR investigations were conducted, revealing that the presence of PI does not hinder the dimerization. (see SI, Figure S3). Also, a slowed addition of EDA as well as the addition in several portions did not prevent the dimerization, which has thus to be considered as a major reason for the low modification yields.

The optimized reaction conditions of **Entry 6c.i** (see Table 2) were transferred to the cyclopropanation of *tert*-butyl diazoacetate (*t*-BDA) (**5**) yielding optimized modification yields of 4–5% (see Table 2, **Entry 6d**). The characterization of the above synthesized modified PIs was accomplished *via* GPC, ^{1}H-NMR, and IR spectroscopy. Details are given in the experimental section and selected results are summed up in Table 3. The reported values of M_n and PDI are both obtained from Gel Permeation Chromatography. The M_n shows in general an increase after modification while the PDI essentially remains the same and is an indication that chain scission associated with many similar postpolymerization reactions did not appear.[19]

The effect of the modification onto the glass transition temperature T_g was investigated by DSC as it is of special importance for the desired tire application (see Table 3). There appears to be a reduction in the segmental mobility due to reduction in rotation around the —CH$_2$— bonds in the backbone of the macromolecules, corresponding to the increase in the number of polar ester groups,[3,39] as the T_g of the virgin PI (**3**) shows an increase from −67°C to −61°C and − 58°C for 5% modified PI, cyclopropanated by EDA (**4**) and *t*-BDA (**5**), respectively. On further increase of modification to 17% (see Table 3, **Entry 6c.i**), the T_g of the cyclopropanated PI shows an increase of ~23°C to −44°C. The regioselectivity of 1,4- and 3,4-PI was also investigated *via* ^{1}H-NMR spectroscopy (details see

Appendix S1) revealing an almost constant ratio between both isomers before and after the modification. This observation indicated that the Cu(I)-catalyzed cyclopropanation of diazo esters on double bonds showed no regioselectivity and is thus in good compliance with the literature.[3] However, a stereoisomeric effect of *cis* and *trans* 1,4-PI could be determined. The average ratio of cis/trans isomers (determined from NMR, see Appendix S1) showed a decrease from 65:25 cis/trans 1,4-PI (2.5) in the case of virgin PI to 55:25 cis/trans 1.4-PI (2.2) after 3–5% modification,. In case of 17% modification yield the ratio was decreased to 50:25 cis/trans 1.4-PI (2), showing a strong preference of *cis*-1,4-PI for the cyclopropanation.

3.2 | Deprotection of cyclopropanated PI

Deprotection experiments were accomplished to transform the cyclopropyl esters bearing PIs into those with free carboxylic group (see Scheme 3), which are finally able to establish ionic interactions or hydrogen bonds. However, in case of the ethyl ester-modified PIs (see Table 2, **Entry 6c.i**), all attempts resulted in very low deprotection when applying for example, sodium hydroxide, phosphoric acid[40] or TFA[41–42] (**8**). Therefore, a change in the diazoester to *t*-BDA(**5**) instead of EDA (**4**) was considered, as the *tert*-butyl groups can be cleaved more efficiently[40–41,43] under weakly acidic conditions.

TABLE 3 Selected examples for characterization data of diazoacetate modified PIs

Entry no.	Reactants	Solvent	Solid content (wt%)	$M_{n,GPC,corr}$[a] (g mol^{-1})	PDI	Percentage modification[b]	T_g (°C)
1	Virgin PI (3)	—	—	2,900	1.1	—	−67
6b.iii	Cat. 2:PI:EDA	Cyclohexane	20	3,100	1.1	5	−61
6c.i	Cat. 2:PI:EDA	DCM	15	3,700	1.1	17	−44
6d.i	Cat. 2:PI:*t*-BDA	DCM	10	3,200	1.1	4	−58
6e	Cat. 1:PI:EDA	1,2-DCE	15	2,600	1.2	5	N/A

Note: The ratio of the catalyst to per double bond of the PI to diazoacetate is set at 0.05:1:2 for all experiments and the ratio of 1,4- / 3,4-PI isomers remains approximately 9.

Abbreviations: DCE, 1,2-dichloroethane; DCM, dichloromethane; EDA, ethyl diazoacetate; PI, poly(isoprene); *t*-BDA, *tert*-butyl diazoacetate.
[a]Correction factor of 0.58 used for M_n obtained by GPC.
[b]Calculated according to the ratio of the signals at the peaks at 5.10 ppm and 4.80–4.63 ppm belonging to 1,4- and 3,4-poly(isoprene) respectively as well as the new peak after modification at 4.10 ppm belonging to the methylene protons of the —CO$_2$*CH$_2$*CH$_3$ moiety of the cyclopropane appearing in ^{1}H-NMR spectroscopy.
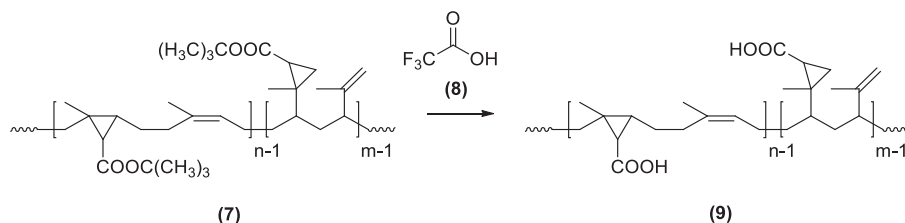
SCHEME 3 Deprotection of (**7**) with trifluoroacetic acid (TFA) (**8**)

To obtain cyclopropane rings substituted with $-CO_2C(CH_3)_3$, t-BDA (**5**) was chosen according to the optimized reaction conditions in the case of EDA (**4**) with DCM as solvent. However, the modification yield with t-BDA was only 4–5% for (**7**) (see Table 2, **Entry 6d**) and is thus much lower compared with EDA in DCM (see Figure 4). A reason for this could be that the PI used is a predominantly cis-polymer and hence modifications in successive repeating units could potentially be hindered by the presence of the much-bulkier $-CO_2$-tert-butyl groups substituted on the cyclopropane rings compared to the $-CO_2$-ethyl groups.

The deprotection of the sample Table 2, **Entry 6d.ii** (**7**) was conducted using TFA (**8**) using a modified
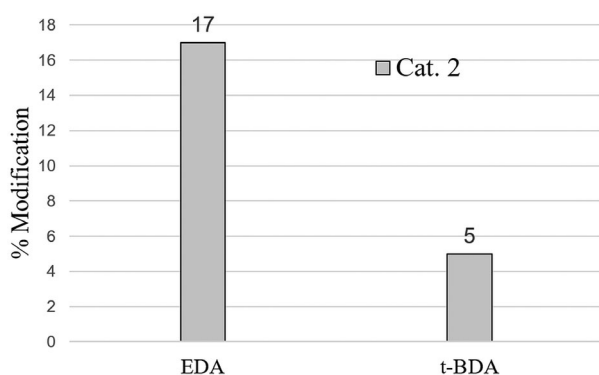

FIGURE 4 Cu(I)-catalyzed cyclopropanation of PI with tert-BDA. The Cat:PI:EDA/t-BDA (**5**) per double bond ratio is 0.05:1:2. The solid content (wt%) of the PI in both the reactions with EDA (**4**) and tert-BDA (**5**) is 15 wt% in DCM. DCM, dichloromethane; EDA, ethyl diazoacetate; PI, poly(isoprene); t-BDA, tert-butyl diazoacetate

method from literature.[42] The deprotected sample (see Figure 5 [**9***]) was a solid powder when compared to the pre-deprotected sample (see Figure 5 [**7***]), which was a viscous liquid. To confirm that the obtained powder was in fact the polymer, GPC was conducted (see Table 4). As can be observed, the M_n values remain firmly in the 2,700–3,200 g/mol range confirming the powder was in fact the modified polymer.

ATR-FTIR-spectroscopy was conducted (see Figure 6) for both, the pre- and post-deprotected samples (**7***) and (**9***) (see Figure 5) respectively. On comparison of the two spectra, two important differences were noted. First is the emergence of a broad peak in the range of 3,300–3,500 cm^{-1} in the postdeprotected sample which could be attributed to the acidic $-OH$. The other is the shift in the peak attributed to the ester ($-COOC(CH_3)_3$) of the modified PI at 1720 cm^{-1} to a lower wavenumber at 1700 cm^{-1} attributed to the deprotected carboxylic acid moiety ($-COOH$).

Preliminary rheology experiments were conducted at different temperatures (see **SI**, Figure S4) with a shear strain of 5%. The sweep could not be performed at temperatures below 130°C as there was slippage at high frequencies and at temperatures above 170°C, decomposition of the deprotected PI was observed.

Further rheology measurements revealed, as expected, a frequency dependency for all PIs, the virgin, the cyclopropyl ester-modified as well as the deprotected COOH PI, as can be seen in Figure 7. At higher frequencies, the individual moduli are higher, and the material appears to be stiffer. A comparison between the virgin and the modified PI at room temperature indicates an increase in the storage modulus by a magnitude of almost
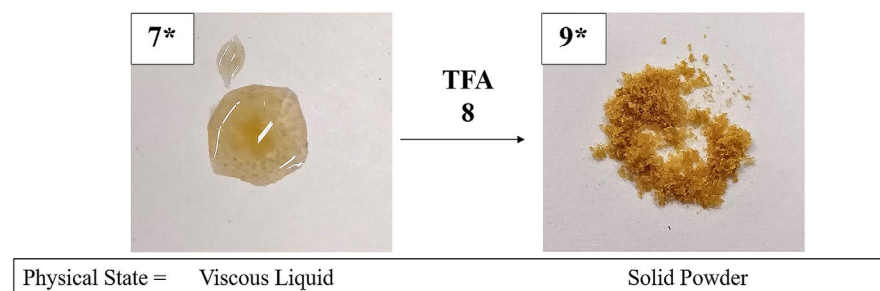

FIGURE 5 Images of t-BDA modified PI (**7**) (see Table 2, **Entry 6d.ii**) before deprotection (**7***) and after deprotection (**9***). (**7***) and (**9***) are the image form of (**7**) and (**9**) as seen in Scheme 3. t-BDA, t-BDA, tert-butyl diazoacetate [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 4 A comparison of $M_{n,GPC}$ pre-(**7***) and postdeprotection (**9***) of t-BDA modified PI

Entry no.	Sample	M_n (GPC) (g/mol)	$M_{n,GPC,corr}$[a] (g/mol) (≈ 0.58)	PDI
1	Virgin PI	5,000	2,900	1.1
2	7*	5,500	3,200	1.1
3	9*	4,700	2,700	1.5

Abbreviations: PI, poly(isoprene); t-BDA, tert-butyl diazoacetate.
[a]Correction factor of 0.58 used for M_n obtained by GPC.
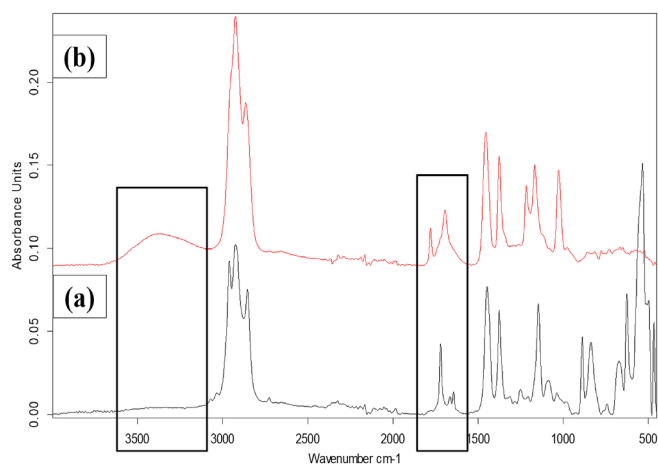
FIGURE 6 ATR-FTIR spectrum of (a) *t*-BDA modified PI (**7***) and (b) modified PI after deprotection (**9***). ATR-FTIR, attenuated total reflection-infrared; PI, poly(isoprene); *t*-BDA, *t*-BDA, *tert-bu*tyl diazoacetate [Color figure can be viewed at wileyonlinelibrary.com]
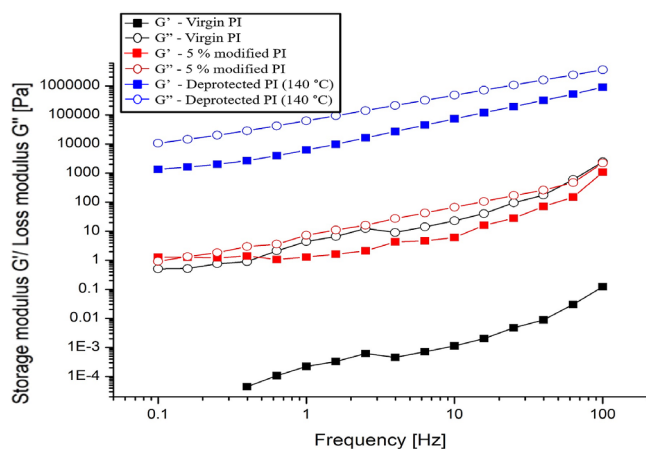

FIGURE 7 Frequency sweep of a virgin, a 5% modified and deprotected PI. PI, poly(isoprene)

10^4, while the loss modulus remains the same, indicating that the cyclopropyl ester modification caused a significant stiffer material even at modification rates of only 5%. At a frequency of 10 Hz, the loss factor tan(δ) is 20,000 and 11 (see **SI**, Table S2) for the virgin PI (3,000 g mol^{-1}) and 5% modified PI, respectively. Hence, the graph clearly indicates that the loss factor tan(δ) is much higher than 1 in the case of virgin PI compared to that of modified PI, indicating that the modulus is dominated by the viscous properties of the material, also indicated by the more liquid behavior of the virgin PI. Similarly, at a frequency of 10 Hz, the loss moduli of the deprotected PI (480,000 Pa) were determined at magnitudes of about 10^4 higher than that of protected PI (68 Pa) (see Figure 7) even at elevated temperatures of 140°C, which were

necessary to melt the COOH-PI by removing the established hydrogen bonds. Comparing the loss modulus of the deprotected PI (480,000 Pa) with that of high molecular weight (HMW) virgin PI of the range 150,000 g/mol (69,000 Pa, Figure S5) show that strong aggregates can be assumed due to hydrogen bond dimers of COOH, finally causing an internal network formation and adopting thus a behavior analogous to the HMW PI. A rigid internal supramolecular network was already established at low modification yields of 5% per individual PI chain, which makes a further deliberate increase in modification yield unnecessary as it would prevent an application of the designed material in tire industry.

4 | CONCLUSION

Cyclopropanations of predominantly *cis*-1,4-PI *via* diazo compounds using Cu(I)-catalysts were conducted, optimizing the reaction parameters while probing solvents of different polarities. Furthermore, variation of the solid content of the PI in selected solvents was also probed. The experimental results showed that higher concentrations increased the modification, with a weakly coordinating polar solvent such as DCM yielding higher modification of up to 17% with 15 wt% solid content compared to the use of the nonpolar cyclohexane with yields up to 4–5% and with 20 wt% solid content. The best result was achieved with the catalyst [(IMes)CuCl] (Cat. **2**) in a molar ratio of 0.05:1 per DB of the PI with the diazoacetates at 2:1 equivalent per double bond of the polymer. The conducted kinetic experiments showed that the highly exothermic reaction was completed within 48 hr at room temperature. However, in respect to potential technical application in the rubber/tire industry, a novel modification with cyclohexane was successfully established.

The deprotection experiments were conducted after the Cu(I)-catalyzed cyclopropanation of the PI with *t*-BDA to obtain cyclopropane rings with tertiary butyl esters. On treating these modified polymers with TFA, deprotection was achieved, yielding cyclopropane rings with attached carboxylic acid moieties as characterized by ATR-FTIR. Rheology experiments revealed that a rigid internal supramolecular network was already established at low modification yields of 5% per individual PI chain. Thus, an introduction of free carboxylic groups along the polymer backbone was successful and enabled a wide variety of applications due to its potential for ionic clustering or hydrogen bonding. The so obtained degree of modification is a first step toward modified polyolefines, aiming to introduce dynamic properties into the rubber after crosslinking in view of the desired self-healing abilities.

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