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Catalytic Cyclopropanation of Polybutadienes

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Keywords

Polybutadiene functionalization; Polar groups; Carbene Addition

Abstract

Catalytic cyclopropanation of commercial 1,2- or 1,4-cis-polybutadiene, respectively, with ethyl diazoacetate catalyzed by [Tp^{Br3}Cu(NCMe)] (Tp^{Br3} = hydrotris(3,4,5-tribromo-

1-pyrazolyl)borate) at room temperature afforded high molecular weight (Mn > 10^5x10^3 g mol^{-1}) side-chain or main-chain, respectively, carboxyethyl cyclopropyl-substituted polymers with variable and controlled degrees of functionalization. Complete functionalization of 1,4-cis-polybutadiene afforded poly[ethylene-alt-(3-ethoxycarbonyl-cyclopro-pene)].Catalytic hydrogenation of residual double bonds of partially cyclopropanated polybutadienes provided access to the corresponding saturated polyolefins. Thermal properties are reported.

Introduction

Catalytic insertion polymerization of ethylene and propylene is employed for the production of more than 60 million tons of polyolefins annually.[1] These polymers are hydrocarbons, without any heteroatom-containing functional groups, such as for example ester moieties. An incorporation of such polar moities is of broad interest, e.g. to increase interactions with polar surfaces, such as metals, or to achieve stability towards hydrocarbon solvents. Albeit significant advances have been achieved most recently with Pd(II) catalysts,[2,3] the incorporation of polar-substituted vinyl co-monomers H_2C=CHX in catalytic insertion polymerization is challenging due to unfavorable interactions of the polar group (X) with the active sites.[4] Thus, ethylene-vinyl acetate copolymers are produced industrially on a large scale by high pressure free-radical polymerization, without microstructure control. Saturated high-performance nitrile-containing elastomers, prepared by free-radical copolymerization of butadiene and acrylonitrile with subsequent post-polymerization hydrogenation may serve as another example.

An alternative to direct incorporation of polar-substituted co-monomers are post-polymerization reactions on insertion polymers, however, for saturated polyolefins modifications are challenging due to the lack of reactive moieties. Most methods were developed for polypropylene and are based on radicals formed by the decomposition of peroxides at high temperature.[5] A disadvantage is chain scission which accompanies these reactions due to the severe conditions. Carbenes, formed by decomposition of diazoacetate at high temperature, can insert into a C-H bond of polyethylene or polypropylene.[6] Examples of catalytic post-polymerization reactions on saturated polyolefins are rare. The oxyfunctionalization of polyethylenes and polypropylenes by metal-based catalysts can afford hydroxyl groups.[7] We have recently reported[8] the functionalization of saturated polybutene and poly(ethylene-1 octene) by insertion of :$CHCO_2Et$ into C-H bonds employing commercially available ethyl diazoacetate (EDA) as the carbene source, using [Tp^{Br3}Cu(NCMe)] as a catalyst precursor (Tp^{Br3} = hydrotris(3,4,5-tribromo-1-pyrazolyl)borate). Degrees of functionalization, which occurred on tertiary and secondary sites, were 4-10 %. A significantly higher reactivity for post-polymerization reactions can be provided by double bonds in hydrocarbon polyolefins or elastomers. Polybutadiene is a particularly attractive substrate as the double bonds present in every repeat unit are suitable for a variety of transformations, and via the polymer microstructure (1,4-cis; 1,4-trans and 1,2-vinyl repeat units) crystallinity and thermal properties can be varied. Thus, post-polymerization modification of polybutadiene by oxidation,[9] epoxidation,[10] hydroboration,[11] hydroformylation[12] and hydrosilylation[13] has been reported.[14] Despite the large number of studies on metal-catalyzed olefin cyclopropanations,[15] the addition of a carbene moiety, from

diazocompounds, to such unsaturated polymers has only been scarcely reported.[16] We are only aware of the addition of dihalocarbenes to unsaturated polymers upon sodium iodide-catalysed decomposition of (trifluoromethyl)phenyl-mercury, at high temperatures.[17]

We now report on saturated, cyclopropyl carboxylate-substituted polyolefins prepared by catalytic cyclopropanation of polybutadienes with variable microstructures under mild conditions.c

Results and Discussion

Functionalization of 1,2-polybutadiene. Early work from our group[18] demonstrated that complexes Tp^xCu (Tp^x = hydrotrispyrazolyborate ligand) catalyze the cyclopropanation of low-molecular-weight olefins with ethyl diazoacetate (EDA) under mild conditions. The catalytic modification of commercialy available polybutadiene semicrystalline polyolefins eq (1) and elastomers, respectively, by this approach was studied.

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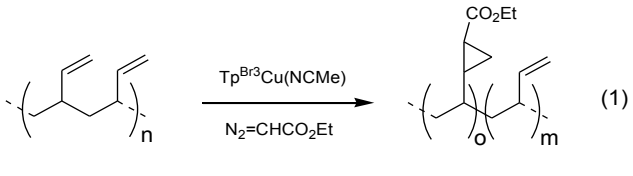

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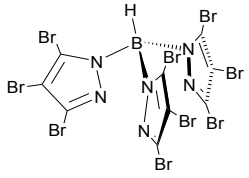
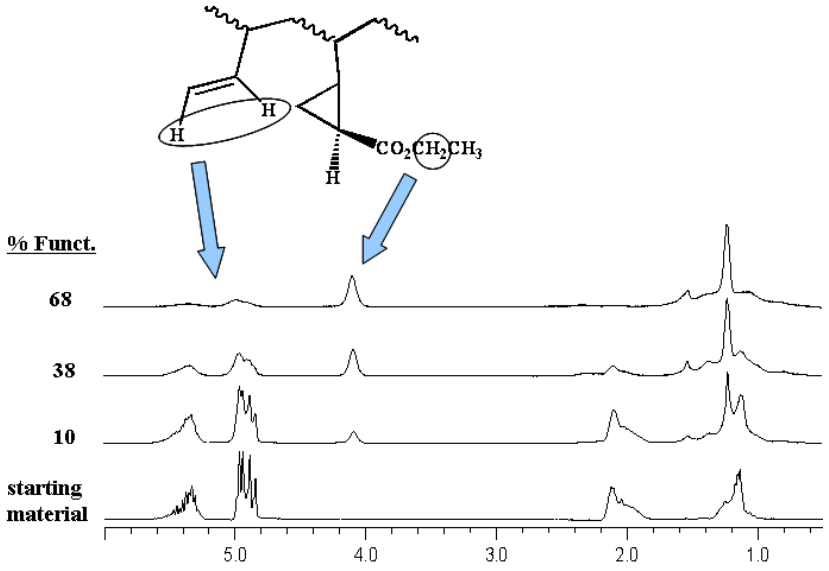


To a solution of 1,2-polybutadiene and catalytic amounts of the complex $Tp^{Br3}Cu(NCMe)$ in dichloromethane, a solution of EDA in the same solvent was added slowly over 15 h by means of a syringe pump. After completion, no EDA was detected by NMR on the reaction mixture. NMR spectroscopy of the isolated polymers reveals their functionalization as well as the degree of incorporation of the carbene unit. Figure 1 shows the ^{1}H NMR spectra of several samples with different degrees of funtionalization. The $CHCO_2CH_2CH_3$ fragments are unambiguously assigned to the resonance centered at 4.10 ppm of the methylene protons and 1.25 ppm of the methyl group. The degree of incorporation can be determined from the relative integrals of the methylene protons of the $CHCO_2Et$ moiety and the olefinic resonances at 5.30 ppm.

Figure 1

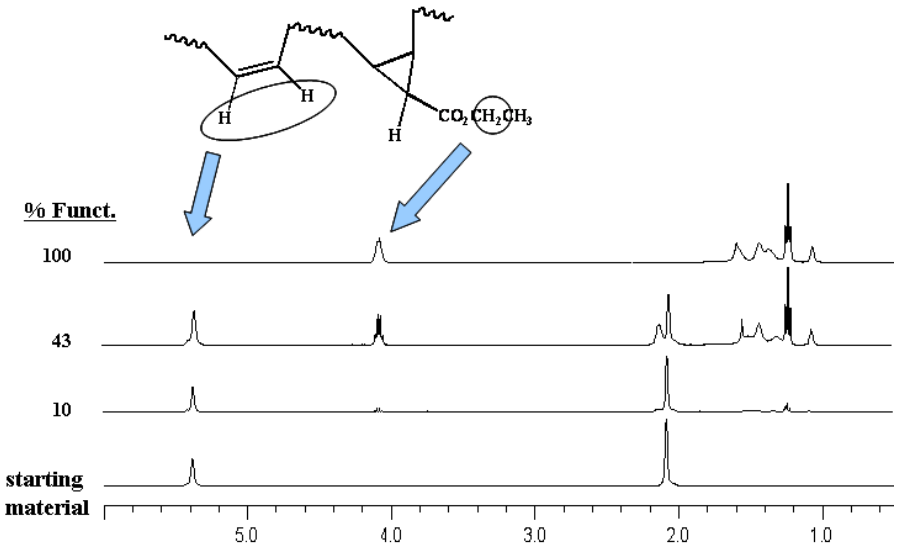
NMR spectra (400 MHz, CDCl3) of cyclopropanated 1,2-polybutadienes with variable degrees of functionalization.



Polymers with degrees of functionalization in the range from 3 to 80 % were obtained, depending on the EDA:polymer double bond ratio (Table 1). A straightforward, linear correlation was observed (Figure 2), allowing for a facile control of polymer composition.

Figure 2

Degree of functionalization (as percentage of cyclopropanated double bonds) of 1,2-polybutadiene with the EDA:polymer double bond molar ratio (catalyst to polymer double bonds 1/ 300).



In view of that molecular weights from GPC are apparent molecular weights determined vs. linear polystyrene standards, and the hydrodynamic behaviour must be expected to vary with functionalization, the molecular weights overall reflect the increase of molecular weight with increasing degree of functionalization.

Table 1. Cyclopropanation of 1,2-polybutadiene.[a]

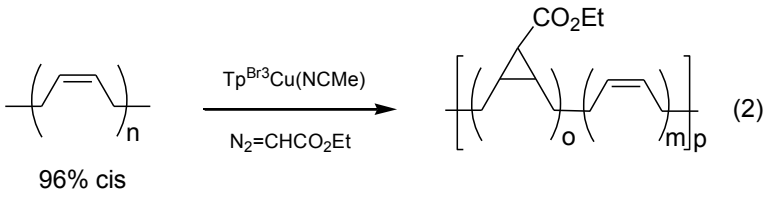
Entry	cat./EDA/PBD	degree of functionalization [%][b]	M_n[c] [10^3 g/mol]	M_w[c] [10^3 g/mol]	M_w/M_n	T_g [°C][d]	T_m [°C][d]
1	n.a.	0	100	245	2.4	-10	96
2	1/30/300	3	93	256	2.8	-4	85
3	1/50/300	4	98	280	2.9	-3	80
4	1/50/150	10	86	273	3.2	6	/
5	1/100/300	16	98	254	2.6	10	/
6	1/200/300	36	133	276	2.1	26	/
7	1/150/150	42	121	267	2.2	30	/
8	1/300/300	43	120	274	2.3	27	/
9	1/600/600	45	121	267	2.2	31	/
10	1/450/300	68	150	293	1.9	43	/
11	1/600/300	80	156	289	1.8	49	/

[a] 0.3 g (5.5 mmol) of polybutadiene, 9.25 µmol $Tp^{Br3}Cu(NCMe)$, 20 mL of CH_2Cl_2; EDA added as solution in 10 mL of CH_2Cl_2 [b]determined by ^1H NMR spectroscopy on the isolated polymer. [c]Determined by GPC in THF at 40° C vs. linear PS standards. [d]determined by DSC.

Furthermore, the essentially unaltered polydispersity can be taken as an evidence of the lack of chain scission, a notorious problem of many post-polymerization reactions. GPC

traces obtained with UV and RI detection are quite similar, indicating that modification occurs uniformly over all molecular weights. Glass transition temperatures increase with increasing degree of modification, which can be related to an increased chain stiffness and reduced mobility by the comparatively bulk carboxyethyl cyclopropyl substituents. At the same time T_m and crystallinity are reduced by comparison to the semicrystalline starting material.

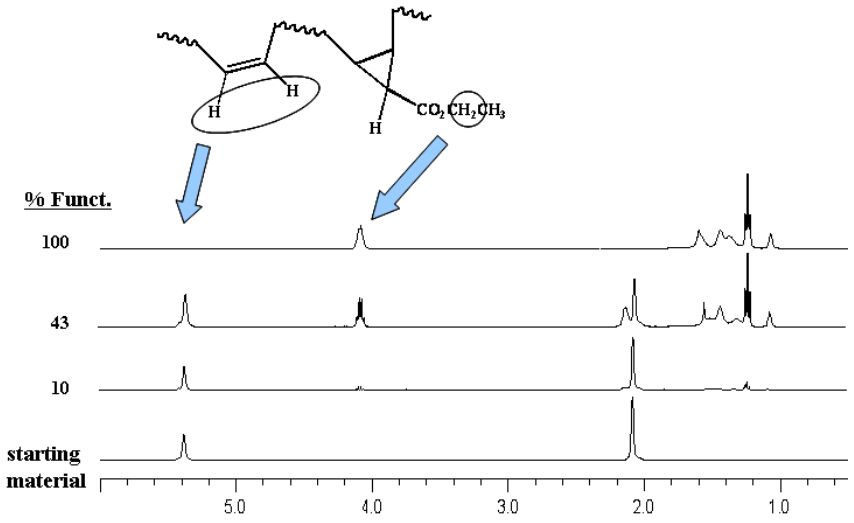
Functionalization of 1,4-polybutadiene. The above methodology was studied as a means for modification of a 1,4-cis-polybutadiene elastomer eq (2) NMR spectroscopy on the isolated polymer again allows for confirmation and quantification of cyclopropanation (Figure 3). Resonances for the carboxylate moiety were observed in similar regions of the NMR spectra related to the aforementioned 1,2-polybutadiene derivatives.



(2)

Figure 3

^{1}H NMR spectra (400 MHz, $CDCl_3$) of cyclopropanated 1,4-polybutadienes with variable degrees of functionalization.



A completely functionalized polymer could be obtained using a two-fold excess of EDA (Table 2). The resulting polymer, poly[ethylene-alt-(3-ethoxycarbonylcyclopropene)], that has not been yet reported, to our knowledge, display molecular weight values of Mn = 360000, Mw = 637000 with Tg = 25ºC. Such degree of incorporation based on converted double bonds of the polymer has only been once in the aforementioned addition of dihalogencarbene units from mercury-based carbene precursors.[17]

The symmetrical nature of poly[ethylene-alt-(3-ethoxycarbonylcyclopropene)] and reduced structural complexity by comparison to only partially substituted products allows for a more detailed NMR analysis (see SI for spectra). ^{1}H/^{13}C chemical shifts of the ethoxy group respectively appear at 1.2/14 ppm for the methyl, 4.1/61 ppm for the methylene, the carbonyl group resonating at 173 ppm. For less functionalized groups,

Table 2. Cyclopropanation of 1,4-cis-polybutadiene.[a]

entry	cat./EDA/PBD	degree of functionali-zation [%][b]	T_g [°C][c]
1	0	0	-81
2	1/200/600	10	-74
3	1/400/600	31	-46
4	1/600/600	46	-21
5	1/900/600	75	4
6	1/1200/600	100	25

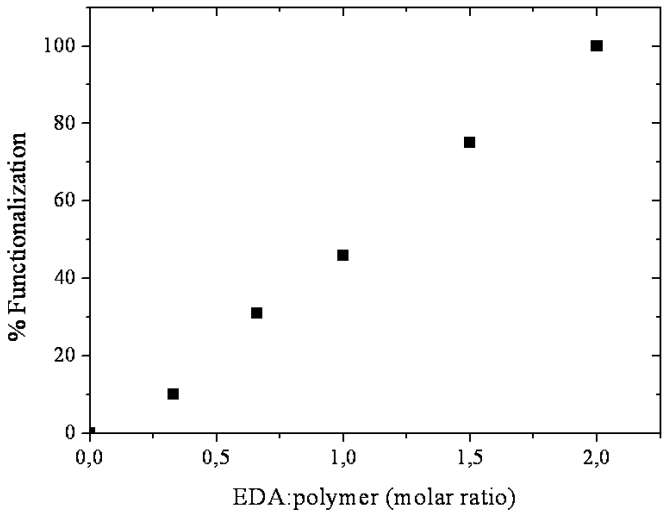
[a]0.3 g (5.5 mmol) of polybutadiene, 9.25 μmol $Tp^{Br3}Cu(NCMe)$, 20 mL of CH_2Cl_2; EDA added as solution in 10 mL of CH_2Cl_2 using a syringe pump [b]Determined by ^1H NMR spectroscopy. [c]Determined by DSC.

relative integration of these resonances and the olefin ones provide the degree of incorporation (see Figure 3). It is worth mentioning that these metal-induced carbene additions from diazocompounds occur throughout a concerted mechanism,[15] therefore retention of the configuration of the C-C double bond is expected. Because of this, and in spite of the lack of NMR data (due to signal broadening) to assess such stereochemistry, is more likely that the cis-configuration has been maintained after functionalization.

The appropriate selection of the catalyst:EDA:polymer ratio allows for a control of the degree of functionalization of the polymer. A quasi-linear correlation between the degree of functionalization and the EDA concentration exists (Figure 4). Similarly as observed for 1,2-polybutadiene, the glass transition temperature increases with the portion of carboxyethyl cyclopropyl-units incorporated.

Figure 4

Correlation of the degree of functionalization of 1,4 polybutadiene and EDA:polymer double bond molar ratio.



Hydrogenation of partially functionalized polymers. Exposure of the partially modified polymers to 50 bar of hydrogen pressure in the presence of Wilkinson's catalyst, [$RhCl(PPh_3)_3$], at 100 ºC resulted in complete conversion of all residual double bonds. This provides access to the saturated polyolefins with variable carboxyethyl cyclopropyl-contents, as exemplified for the side-chain substituted polymers obtained from 1,2-polybutadiene (Table 3).

Cleavage of the cyclopropane ring does not occur under these hydrogenation conditions.

Table 3. Hydrogenation of cyclopropanated 1,2-polybutadienes.[a]

Entry	[%][b]	M_n[c]	M_w[c]	M_w/M_n[c]	T_g [°C][d]
1	0	100	245	2.4	-30
2	4	64	144	2.3	-28
3	10	57	121	2.1	-20
4	16	160	267	1.7	-10
5	38	98	172	1.8	11
6	39	100	216	2.2	14
7	68	134	228	1.7	39
8	80	144	247	1.7	44

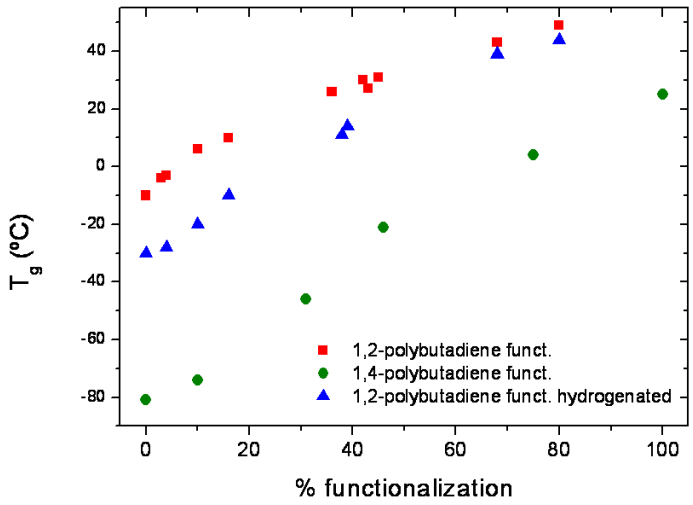
[a]0.1 g of functionalized polymer, $[RhCl(PPh_3)_3]$ (6 μmol), PPh_3 (114 μmol), 20 mL of toluene; 50 atm of H_2; 100°C; 20 h. [b] Degree of functionalization determined by ^{1}H NMR spectroscopy. [c]Determined by GPC in THF at 40°C vs. linear PS standards. [d] Determined by DSC.

This is also evidenced independently and straightforwardly by exposure of the completely functionalized poly[ethylene-alt-(3-ethoxycarbonylcyclopropene)] to the hydrogenation conditions. No alteration of the ^{1}H NMR spectrum is observed, and the signals of the cyclopropane remain (see SI).

Glass transition temperatures of the saturated polymers are slightly higher than the corresponding unsaturated starting materials, and cover the range from -30ºC to +40ºC (Figure 5 and Table 3). As for the unsaturated polymers, Tg increases with the degree of carboxyethyl cyclopropyl-substitution.

Figure 5

Correlation of glass transition temperature with polymer composition



Experimental

Materials and general considerations. All manipulations were carried out under a argon atmosphere using standard Schlenk techniques. Solvents were dried and degassed before use with a MBRAUN SPS system. NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer on $CDCl_3$ solutions. NMR assignments were confirmed by ^{1}H, ^{13}C, 1D and 2D homo and heteronuclear experiments. 1,4-cis-polybutadiene Buna® CB 24 from Lanxess with a 1,4-cis-content of 96% and syndiotactic 1,2-polybutadiene JSR RB® 820 from Japan Synthetic Rubber with a 1,2-content of 92% were employed. Ethyl

diazoacetate was purchased from Aldrich. [Tp^{Br3}Cu(NCMe)] was prepared according to literature.[19] GPC was carried out on a Polymer Laboratories PL-GPC 50 instrument with two PLgel 5 μm MIXED-C columns in THF at 40°C against polystyrene standards. DSC was carried out on a Netzsch F1 instrument, in the range from -100 to +150 at 10 K min^{-1} heating/cooling rate (T_g and T_m given are from the secondary heating curves). Both polymers of Table 2, entry 1 and 2, were measured with 30 K min-^{1}.

Catalytic functionalization of polybutadienes. The polymer (0.3 g, 5.5 mmol) was dissolved in 20 mL of CH_2Cl_2 in a Schlenk flask, and Tp^{Br3}Cu(NCMe) (0.00925 mmol) was added to the stirred solution. By means of a syringe pump, a solution of EDA in 10 mL of CH_2Cl_2 was added slowly to the polymer solution in 15 hours At the end of the addition period, no EDA was detected in solution by NMR studies. The solution was concentrated to 10 mL in vaccuo. 50 mL of methanol were added to precipitate the polymer. Filtration, further washing with 2 x 30 mL of methanol, and drying under vacuum afforded the product polymer in >85 - 90% yield.

Analytical data for poly[ethylene-alt-(3-ethoxycarbonylcyclopropene)]: ^{1}H NMR (400 MHz, 20 ^{o}C, $CDCl_3$): 1.08 (br s, *CH*CO_2Et), 1.23 (t, OCH_2CH_3), 1.38 (br s, $CH_cH_dCH_cH_d$), 1.42 (br s, *CH* $CHCO_2Et$), 1.60 (br s, $CH_cH_dCH_cH_d$), 4.05 (br s, OCH_2CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, 20 ^{o}C, $CDCl_3$): 14.3 (OCH_2CH_3), 26.8 ($CHCO_2Et$), 27.2 ($-CH_a$), 27.4, 27.3 (CH_2CH_2), 60.3 (OCH_2CH_3), 174.1 (CO_2Et).

Hydrogenation of functionalized polymers. 0.1 g of the functionalized polymer obtained as above were dissolved in 20 mL of toluene and placed into a Schlenk flask along with Wilkinson's catalyst (0.006 mmol) and PPh_3 (0.114 mmol). The mixture was stirred to obtain a homogeneous solution, and was then transferred into a pressure vessel and pressurized to 50 atm of H_2. The mixture was stirred at 100°C for 20 h. After cooling to room temperature, the volume was reduced to 10 mL and methanol was added (50 mL) to induce the separation of the solid polymer. Filtration, washing and drying afforded the hydrogenated, functionalized polymer in ca. 70 % yield.

Conclusion

Post-polymerization cyclopropanation of polybutadienes, introducing polar carboxyethyl cyclopropyl units, occurs under mild conditions with $Tp^{Br3}Cu(NCMe)]$ as a catalyst precursor. This was demonstrated for semicrystalline 1,2-polybutadiene as a starting material, resulting in side-chain functionalization, as well as a 1,4-cis-polybutadiene, resulting in main-chain substitution. Degrees of functionalization can be varied over a wide range in a controlled fashion. Complete conversion of 1,4-polybutadiene affords the novel poly[ethylene-alt-(3-ethoxycarbonylcyclopropene)]. This is noteworthy in view of the often limited conversions in post-polymerization reactions. No evidence of a conceivable chain session, problematic in many post-polymerization reactions, was observed. Partially functionalized polymers could be converted completely to the corresponding saturated polyolefins by catalytic hydrogenation. Introduction of the

comparatively bulky polar carboxyethyl cyclopropyl groups results in increased glass transition temperatures in all cases.

Acknowledgements

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Graphical Abstract

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Graphical Abstract 1