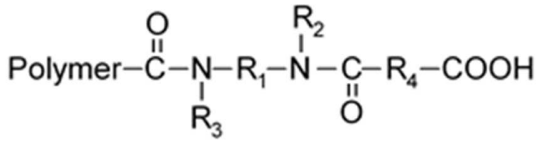
Patent claims:

1. A carboxy-terminated polymer according to general formula (I),



(I),

wherein

the "polymer" is a diene rubber and contains at least one carbon-carbon double bond and wherein the polymer is obtainable by a polymerization reaction comprising the homopolymerization or copolymerization of one or more diene selected from 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethylbutadiene, 1-phenyl-1,3-butadiene or 1,3-hexadiene and a combination thereof;

R_2, R_3 are identical or different and represent saturated or unsaturated organic radicals which may contain one or more heteroatoms selected from the group consisting of O, N, S and Si; and

R_1, R_4 are identical or different and represent saturated or unsaturated divalent organic radicals which, in addition to C and H, may contain one or more heteroatoms another selected from the group consisting of O, N, S and Si.

~~2. The carboxyterminated polymer according to claim 1, wherein the "polymer" is obtainable by~~

~~- homo- or copolymerization of dienes; or~~

~~- copolymerization of dienes with vinylaromatic monomers.~~

2~~3~~. The carboxy-terminated polymer according to claim 1~~2~~, wherein the "polymer" is obtainable by a

– homo- or copolymerization of 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-butadiene, 1-phenyl-1,3-butadiene or 1,3-hexadiene; or

– a copolymerization of

(i) 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethylbutadiene, 1-phenyl-1,3-butadiene, ~~and/or~~ 1,3-hexadiene or a combination thereof with

(ii) styrene, o-, m- and/or p-methylstyrene, p-tert-butylstyrene, methylstyrene, vinylnaphthalene, divinylbenzene, trivinylbenzene, ~~and/or~~ divinylnaphthalene or a combination thereof.

34. The carboxy-terminated polymer according to any one of the preceding claim~~s 3~~, wherein the ~~"~~polymer~~"~~ is obtainable by a copolymerization of 1,3-butadiene with styrene; or of isoprene with styrene.~~; preferably 1,3-butadiene with styrene~~.

~~5. The carboxyterminated polymer according to any of the preceding claims, wherein~~

~~R_2, R_3 are identical or different and represent saturated or unsaturated organic radicals which may contain one or more heteroatoms independently of one another selected from the group consisting of O, N, S and Si; preferably $-CH_3$; and~~

~~R_1, R_4 are identical or different and represent saturated or unsaturated divalent organic radicals which, in addition to C and H, may contain one or more heteroatoms independently of one another selected from the group consisting of O, N, S and Si; preferably R_1 means $-CH_2-CH_2-$ and R_4 is selected from $-CH_2-CHC_kH_{2k+1}-$ wherein k is an integer of from 8 to 16; $-CH_2CH((CH_2)_{1-5}Si(OC_1-C_4\text{-alkyl})_3)$; $-CH=CC_1-C_4\text{-alkyl}-$, and $-(CH_2)_{2-4}-$; more preferably R_1 means $-CH_2-CH_2-$ and R_4 is selected from $-CH_2-CHC_{12}H_{23}-$, $-CH_2CH(CH_2CH_2CH_2Si(OCH_3)_3)$, $-CH=CCH_3-$, and $-CH_2CH_2-CH_2-$.~~

46. The carboxy-terminated polymer according to any one of the preceding ~~of~~ claims ~~1 to 4~~, wherein

- R_1 is selected from the group consisting of

  (i) a $-C_1-C_6$-alkylene-, that is saturated or unsaturated and~~,~~ that is either unsubstituted, mono- or polysubstituted;

  (ii) a $-C_1-C_6$-heteroalkylene-, that is saturated or unsaturated and that is~~,~~ unsubstituted, mono- or polysubstituted; ~~and~~

  (iii) a 6 to ~~-~~14-membered arylene~~,~~ that is unsubstituted, mono- or polysubstituted;

  ~~and/or~~

- R_2 is selected from the group consisting of

(i) a -C_1-C_{24}-alkyl, that is saturated or unsaturated and~~,~~ that is unsubstituted, mono- or polysubstituted; or

(ii) a -C_1-C_{24}-heteroalkyl, that is saturated or unsaturated and~~,~~ that is unsubstituted, mono- or polysubstituted;

(iii) a 6 to~~-~~24-membered aryl, that is unsubstituted, mono- or polysubstituted, wherein said 6 to~~-~~24-membered aryl is optionally connected through a -C_1-C_6-alkylene- or a -C_1-C_6-heteroalkylene-, which in each case is saturated or unsaturated~~,~~ and which is unsubstituted, mono- or polysubstituted;

(iv) a 5 to~~-~~24-membered heteroaryl, that is unsubstituted, mono- or polysubstituted~~,~~; wherein said 5 to~~-~~24-membered heteroaryl is optionally connected through a -C_1-C_6-alkylene- or a -C_1-C_6-heteroalkylene-, which in each case is saturated or unsaturated and~~,~~ which is unsubstituted, mono- or polysubstituted;

(v) ~~3~~a 3 to ~~-~~24-membered cycloalkyl, that is saturated or unsaturated and~~,~~ that is unsubstituted, mono- or polysubstituted~~,~~; wherein said 3 to~~-~~24-membered cycloalkyl is optionally connected through a -C_1-C_6-alkylene- or a -C_1-C_6-heteroalkylene-, which in each case is saturated or unsaturated and~~,~~ which is unsubstituted, mono- or polysubstituted; and

(vi) a 3 to ~~-~~24-membered heterocycloalkyl, that is saturated or unsaturated~~,~~ and that is unsubstituted, mono- or polysubstituted~~,~~; wherein said 3 to ~~-~~24-membered heterocycloalkyl is optionally connected through -C_1-C_6-alkylene- or -C_1-C_6-heteroalkylene-, which in each case is saturated or unsaturated and~~,~~ which is unsubstituted, mono- or polysubstituted;

~~and/or~~

- R_3 is selected from the group consisting of

(i) -C_1-C_{24}-alkyl, that is saturated or unsaturated and~~,~~ that is unsubstituted, mono- or polysubstituted;

(ii) -C_1-C_{24}-heteroalkyl, that is saturated or unsaturated and~~,~~ that is unsubstituted, mono- or polysubstituted;

(iii) 6 to~~-~~24-membered aryl, that is unsubstituted, mono- or polysubstituted, wherein said 6 to ~~-~~24-membered aryl is optionally connected through a -C_1-C_6-alkylene- or a -C_1-

C_6-heteroalkylene-, which in each case is saturated or unsaturated and, that is unsubstituted, mono- or polysubstituted;

(iv) a 5 to 24-membered heteroaryl, that is unsubstituted, mono- or polysubstituted, wherein said 5- to 24-membered heteroaryl is optionally connected through a -C_1-C_6-alkylene- or a -C_1-C_6-heteroalkylene-, which in each case is saturated or unsaturated and, which is unsubstituted, mono- or polysubstituted;

(v) a 3 to 24-membered cycloalkyl, that is saturated or unsaturated and, that is unsubstituted, mono- or polysubstituted, wherein said 3 to 24-membered cycloalkyl is optionally connected through a -C_1-C_6-alkylene- or a -C_1-C_6-heteroalkylene-, which in each case is saturated or unsaturated and, which is unsubstituted, mono- or polysubstituted; and

(vi) a 3 to 24-membered heterocycloalkyl, that is saturated or unsaturated and, that is unsubstituted, mono- or polysubstituted, wherein said 3 to 24-membered heterocycloalkyl is optionally connected through a -C_1-C_6-alkylene- or a -C_1-C_6-heteroalkylene-, which in each case is saturated or unsaturated and, which is unsubstituted, mono- or polysubstituted;

~~and/or~~

- R_4 is selected from the group consisting of

(i) a -C_1-C_6-alkylene-, that is saturated or unsaturated and, that is unsubstituted, mono- or polysubstituted;

(ii) a -C_1-C_6-heteroalkylene-, that is saturated or unsaturated and, that is unsubstituted, mono- or polysubstituted; and

(iii) a 6 to 14-membered arylene, that is unsubstituted, mono- or polysubstituted;

wherein "*mono- or polysubstituted*" ~~in each case independently~~ means substituted with one substituent, in case of “monosubstituted”, or with more than one substituent, in case of “polysubstituted”, and wherein the ~~more~~ substituent~~s~~ are selected independently ~~of one another selected~~ from the group consisting of -F, -Cl, -Br, -I, -CN, =O, -CF_3, -CF_2H, -CFH_2, -CF_2Cl, -$CFCl_2$, a -C_1-C_{18}-alkyl that is, saturated or unsaturated and, that is unsubstituted, and a -C_1-C_{18}-heteroalkyl that is, saturated or unsaturated and, that is unsubstituted.

5~~7~~. The carboxy-terminated polymer according to any one of the preceding claims ~~claim 6,~~ wherein

- R_1 is ~~(i)~~ a -C_1-C_6-alkylene- that is~~,~~ saturated or unsaturated and~~,~~ that is unsubstituted; ~~or (ii) -C_1-C_3-alkylene, saturated or unsaturated, unsubstituted; and/or~~
- R_2 is ~~(i)~~ a -C_1-C_6-alkyl that is ~~,~~ saturated or unsaturated and~~,~~ that is unsubstituted; ~~or (ii) -C_1-C_2-alkyl, saturated or unsaturated, unsubstituted; and/or~~
- R_3 is ~~(i)~~ a -C_1-C_6-alkyl that is~~,~~ saturated or unsaturated and~~,~~ that is unsubstituted; ~~or (ii) -C_1-C_2-alkyl, saturated or unsaturated, unsubstituted; and/or~~and
- R_4 is ~~(i)~~ a -C_1-C_6-alkylene- that is~~,~~ saturated or unsaturated and~~,~~ that is either unsubstituted, mono- or polysubstituted; ~~or (ii) -C_1-C_3-alkylene-, saturated or unsaturated, unsubstituted, mono- or polysubstituted~~;

wherein ~~in each case~~ "*mono- or polysubstituted*" means substituted with one substituent in case of “monosubstituted” or more than one substituent in case of “polysubstituted” and wherein the substituents are ~~s~~ selected independently ~~of one another selected~~ from the group consisting of

-F, -Cl, -Br, -I, -CN, -CF_3, -CF_2H, -CFH_2, -CF_2Cl, -$CFCl_2$,

a -C_1-C_{18}-alkyl that is~~,~~ saturated or unsaturated and~~,~~ that is unsubstituted, and

a -C_1-C_{18}-heteroalkyl that is~~,~~ saturated or unsaturated and~~,~~ that is unsubstituted.

6. The carboxy-terminated polymer according to any one of the preceding claims, wherein

- R_1 is a -C_1-C_6-alkylene- that is saturated or unsaturated and that is unsubstituted;
- R_2 is a -C_1-C_6-alkyl that is saturated or unsaturated and that is unsubstituted;
- R_3 is a -C_1-C_6-alkyl that is saturated or unsaturated and that is unsubstituted; and
- R_4 is a -C_1-C_6-alkylene- that is saturated or unsaturated and that is either unsubstituted, mono- or polysubstituted;

wherein "*mono- or polysubstituted*" means substituted with one substituent in case of “monosubstituted” or more than one substituent in case of “polysubstituted” and wherein the substituents are selected independently from the group consisting of a -C_1-C_{18}-alkyl that is

saturated and unsubstituted or a -C_1-C_6-alkyl-Si(O-C_1-C_6-alkyl)$_3$, wherein in each case the -C_1-C_6-alkyl is saturated or unsaturated.

7~~8~~. The carboxy-terminated polymer according to any of the preceding claims, wherein

~~-~~ the "~~"~~polymer~~"~~ is obtainable by a copolymerization of 1,3-butadiene with styrene and wherein;

- R_1 is a -C_1-C_3-alkylene-, that is saturated or unsaturated and that is~~,~~ unsubstituted; ~~preferably -CH_2CH_2-;~~
- R_2 is a -C_1-C_2-alkyl, that is saturated or unsaturated and that is~~,~~ unsubstituted~~; preferably -CH_3~~;
- R_3 is a -C_1-C_2-alkyl that is~~,~~ saturated or unsaturated and that is~~,~~ unsubstituted;~~ preferably -CH_3~~; and
- R_4 is a -C_1-C_3-alkylene- that is~~,~~ saturated or unsaturated and that is~~,~~ unsubstituted, mono- or polysubstituted; ~~preferably R_4 is selected from -CH_2-CHC_kH_{2k+1}- wherein k is an integer of from 8 to 16; -$CH_2CH((CH_2)_{1-5}Si(OC_1$-$C_4$-alkyl)$_3$); -CH=CC$_1$-$C_4$-alkyl-, and -$(CH_2)_{2-4}$-; more preferably R_4 is selected from -CH_2-$CHC_{12}H_{23}$-, -$CH_2CH(CH_2CH_2CH_2Si(OCH_3)_3)$, -CH=CC$H_3$-, and -$CH_2CH_2$-$CH_2$-;~~

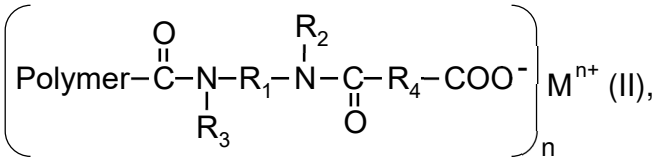
wherein "*mono- or polysubstituted*" means substituted with one substituent in case of “monosubstituted” or more than one substituent in case of “polysubstituted” and wherein the substituents are selected independently from the group consisting of ~~wherein in each case "*mono- or polysubstituted*" means substituted with one or more substituents independently of one another selected from~~ a -C_1-C_{18}-alkyl that is~~,~~ saturated or unsaturated and that is~~,~~ unsubstituted, and ~~a -C_1-C_{18}-heteroalkyl, saturated or unsaturated, unsubstituted; preferably selected from -C_1-C_{18}-alkyl, saturated or unsaturated, unsubstituted or~~ -C_1-C_6-alkyl-Si(O-C_1-C_6-alkyl)$_3$ that is saturated or unsaturated~~,~~ and that is unsubstituted.

8. The carboxy-terminated polymer according to any one of the preceding claims, wherein the polymer is obtainable by a copolymerization of 1,3-butadiene with styrene and wherein

- R_1 is a -C_1-C_3-alkylene- that is saturated or unsaturated and that is unsubstituted;
- R_2 is a -C_1-C_2-alkyl that is saturated or unsaturated and that is unsubstituted;
- R_3 is -C_1-C_2-alkyl that is saturated or unsaturated and that is unsubstituted; and

- R_4 is selected from $-CH_2-CHC_kH_{2k+1}-$, $-CH_2CH((CH_2)_{1-5}Si(OC_1-C_4\text{-alkyl})_3-$, $-CH=C(C_1-C_4\text{-alkyl})-$, and $-(CH_2)_{2-4}-$, wherein k is an integer of from 8 to 16.

9. The carboxy-terminated polymer according to any of the preceding claims, being ~~which is~~ present as a carboxylate according to general formula (II),



(II),

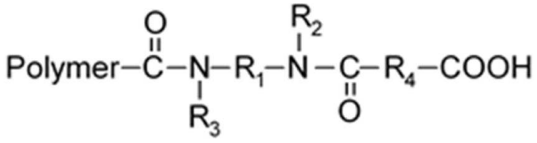
wherein

~~"~~polymer~~"~~, R_1, R_2, R_3 and R_4 are as defined in any one of the preceding claims;

n is an integer from 1 to 4; and

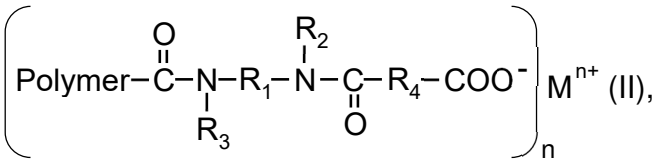
M is a metal or semi-metal of valency 1 to 4 selected from ~~, preferably~~ Li, Na, K, Mg, Ca, Zn, Fe, Co, Ni, Al, Nd, Ti, Sn, Si, Zr, V, Mo or W.

10. A method for the preparation of a carboxy-terminated polymer according to general formula (I),



(I),

or ~~of a carboxylate according to~~ general formula (II),

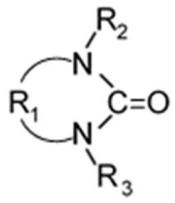


(II),

the method comprising ~~the following steps of~~:

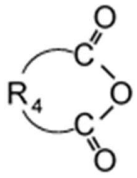
(a) providing a ~~"~~polymer~~"~~ containing at least one carbon-carbon double bond;

(b) providing a cyclic urea derivative of the general formula (III)



(III);

(c) providing a cyclic carboxylic anhydride of the general formula (IV)



(IV);

(d) adding the cyclic urea derivative of general formula (III) to the "polymer" as a first functionalization reagent to form a functionalized polymer intermediate; and

(e) subsequently adding the cyclic carboxylic anhydride of the general formula (IV) to the functionalized polymer intermediate as a second functionalization reagent to form the carboxy-terminated polymer according to general formula (I) or ~~the carboxylate according to general formula~~ (II);

wherein "polymer", n, M, R_1, R_2, R_3 and R_4 are as defined in any one of claims 1 to 9.

11. The method according to claim 10, wherein step (a) is performed by

- an anionic solution polymerization, or
- a polymerization using a coordination catalyst, wherein the coordination catalyst is preferably a Ziegler-Natta catalyst or a monometallic catalyst system.

12. The method according to claim 10 or 11, wherein step (a) is performed in the presence of

- a solvent, wherein the solvent is preferably selected from the group consisting of cyclohexane, methylcyclopentane, n-hexane and mixtures thereof; and/or
- an initiator, which is preferably n-butyllithium or sec-butyllithium.

13. The method according to any of claims 10 to 12, wherein step (a) is performed within a period of 10 minutes to 8 hours, preferably 20 minutes to 4 hours.

14. The method according to any of claims 10 to 13, which comprises the additional step(s) of adding

    (f) a coupling reagent before, together with or after addition of the cyclic urea derivative of general formula (III), wherein the coupling reagent is preferably selected from the group consisting of silicon tetrachloride, methyltrichlorosilane, dimethyldichlorosilane, tin tetrachloride, dibutyltin dichloride, tetraalkoxysilanes, ethylene glycol diglycidyl ether and 1,2,4-tris(chloromethyl)benzene; and/or

    (g) an antioxidant after the cyclic urea derivative of the general formula (III) and the cyclic carboxylic anhydride of general formula (IV) have been added, wherein the antioxidant is preferably selected from the group consisting of sterically hindered phenols, aromatic amines, phosphites and thioethers; and/or

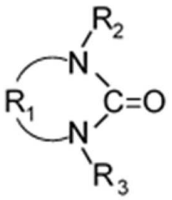
    (h) an extender oil, wherein the extender oil is preferably selected from the group consisting of a TDAE (Treated Distillate Aromatic Extract)-, a MES (Mild Extraction Solvates)-, a RAE (Residual Aromatic Extract)-, a TRAE (Treated Residual Aromatic Extract)-, a naphthenic and a heavy naphthenic oil; and/or

    (i) a filler, which is preferably carbon black or silica; and/or

    (j) rubbers and/or rubber additives.

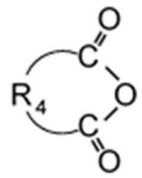
~~15. Successive use of~~

~~- a cyclic urea derivative of the general formula (III) as a first functionalization reagent~~



~~(III); and~~

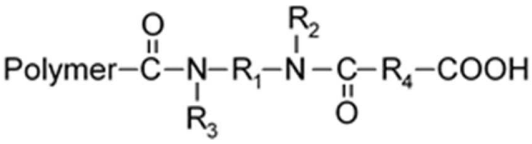
~~- a cyclic carboxylic anhydride of the general formula (IV) as a subsequent second functionalization reagent~~



(IV);

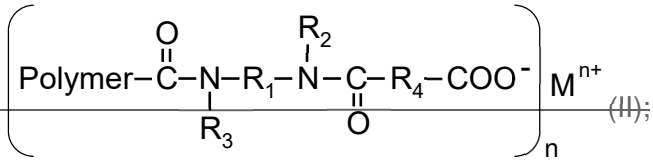
for the preparation of a

- carboxyterminated polymer according to general formula (I),



(I); or

- a carboxylate according to formula (II),



(II);

wherein in each case "polymer", n, M, R_1, R_2, R_3 and R_4 are as defined in any of claims 1 to 9.

15. A molded article, preferably a tire, prepared by vulcanizing a vulcanizable composition comprising the carboxy-terminated polymer of any one of claims 1 to 9.