(REMP) is a powerful means for preparing cyclic polymers, where ruthenium (Ru)-based metathesis catalysts are used to produce cyclic polymers directly from cyclic monomers. Because cyclic polymers remain intact during the entire process, REMP can generate high MWs cyclic polymers in concentrated solution or in bulk. Among the cyclic polymers that have been prepared are poly(valerolactone), poly(caprolactone), poly(t-butyl acrylate), polystyrene, poly(*N*-isopropyl acrylamide), poly(azo-methyl acrylate), poly(isobutylene), poly(4-vinylbenzyl-carbazole), poly(methylmethacrylate) poly(tetrahydrofuran), poly(lactide), poly(ethylene oxide), poly(cyclooctene), poly(5-acetoxy-1-cyclooctene), poly(cyclododecatriene), poly(exo-5-norbornene-carboxylic acid pentafluorophenol ester), poly(butyrolactone), poly(*N*-carboxyanhydride), poly(styrene-co-methyl acrylate), poly(methylacrylate), poly(thiirane), poly(methylene), poly(norbornene)-*g*-polystyrene, poly(norbornene)-*g*-poly(lactide), poly(norbornene)-*g*-poly(n-butyl acrylate), poly(norbornene)-*g*-poly(ethylene oxide) and poly(*N*-carboxyanhydride)-*g*-poly(ethylene oxide).

[0006] Recently, Veige *et al*. US Patent No. 9,206,266 has demonstrated the polymerization of acyclic alkynes to cyclic polyalkenes, for example, cyclic poly(phenylacetylene), using a pincer ligand supported metallocycloalkylene tungsten complex. As the initial and terminal ends are bound to the complex, chain-termination and chain transfer occurs with coupling of the initial and terminal ends to form a cyclic topology. Polymerization occurs in high yield and high selectivity of cyclization. Extension of this technology to polyalkanes, such as the production of cyclic polypropylene, is desirable.

SUMMARY

[0006a] In one aspect, the present disclosure refers to a macrocyclic polyalkene copolymer, comprising a conjugated polyalkene having no chain ends and in the form of a macrocycle, comprising at least two different repeating units have the structure -RC=CR- where R is independently: H; a substituted or unsubstituted C_1 to C_{30} alkyl, provided that when all R are an unsubstituted C_1 to C_{30} alkyl, at least one R is not a C_4, C_6, C_7, or C_{13} alkyl; substituted or unsubstituted C_3 to C_{30} alkenyl having one or more alkene bonds where a plurality of alkene bonds can be non-conjugated, conjugated, or a mixture thereof; or where two R groups are combined as a C_8-C_{30} cycloalkene where the alkylene portion of the cycloalkene is substituted or unsubstituted and/or interrupted one or more times with O, NR',

C(O), C(O)O, and/or C(O)NR", where R' and/or R", when present are each independently H, $C_{1\text{-}30}$ alkyl, or C_3 to C_{30} alkenyl.

[0006b] In another aspect, the present disclosure refers to a macrocyclic polyalkane or macrocyclic poly(alkane-co-alkene), comprising alkane repeating units have the structure -RHC-CHR- and, optionally, alkene repeating units have the structure -RC=CR- or–$C(=CR_2)$-, where, if present, the R of the -RC=CR- alkene repeating units are the same as the R units of at least one of the alkane repeating units, and where R is independently: H; a substituted or unsubstituted C_1 to C_{30} alkyl, or, when absent an alkene repeating unit or comprising exclusively one unsubstituted alkane repeating units or a copolymer with $–H_2C\text{-}CH_2$- repeating units, R is $C_{1\text{-}3}$, C_5, $C_{8\text{-}12}$, or $C_{14\text{-}30}$; substituted or unsubstituted C_3 to C_{30} alkenyl having one or more alkene bonds where a plurality of alkene bonds can be non-conjugated, conjugated, or a mixture thereof; or where two R groups are combined as a C_8-C_{30} cycloalkane and/or cycloalkene where the alkylene portion of the cycloalkane and/or alkene is substituted or unsubstituted and/or interrupted one or more times with O, NR', C(O), C(O)O, and/or C(O)NR", where R' and/or R", when present, are each independently H, $C_{1\text{-}30}$ alkyl, C_3 to C_{30} alkenyl.

[0006c] In yet another aspect, the present disclosure refers to a method of forming a macrocyclic polyalkane or a macrocyclic poly(alkane-co-alkene) disclosed herein comprising:

reacting a macrocyclic polyalkene and hydrogen in the presence of a hydrogenation catalyst to form the polyalkane or poly(alkane-co-alkene); and

isolating the macrocyclic polyalkane or a macrocyclic poly(alkane-co-alkene).

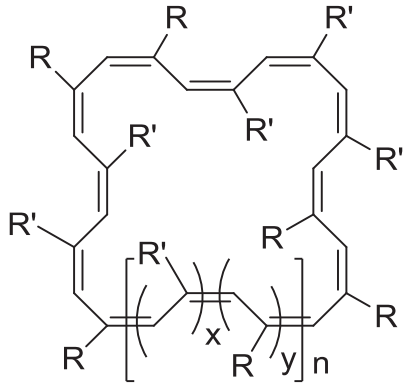
[0006d] In a further aspect, the present disclosure refers to a method of forming a macrocyclic polyalkane or a macrocyclic poly(alkane-co-alkene) disclosed herein comprising:

reacting a macrocyclic poly(cycloalkene) with an excess of an alkene and an olefin metathesis catalyst thereby forming a macrocyclic poly(alkane-co-alkene) comprising vicinal $–C(=CR_2)$- groups; and

optionally isolating the macrocyclic polyalkane or the macrocyclic poly(alkane-co-alkene) comprising –C(=CR_2)- groups.

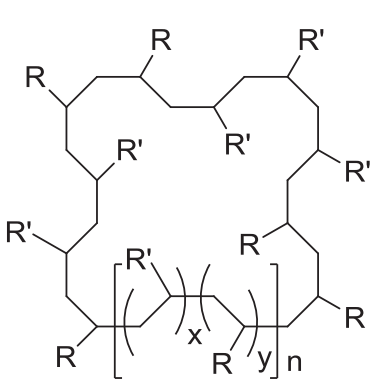
[0007] Provided herein are macrocyclic polyalkene copolymers that are a conjugated polyalkene having no chain ends and in the form of a macrocycle, comprising at least two different repeating units have the structure -RC=CR-. The R groups are independently: H; a substituted or unsubstituted C_1 to C_{30} alkyl, provided that when all R are an unsubstituted C_1 to C_{30} alkyl, at least one R is not a C_4, C_6, C_7, or C_{13} alkyl; substituted or unsubstituted C_3 to C_{30} alkenyl having one or more alkene bonds where a plurality of alkene bonds can be non-conjugated, conjugated, or a mixture thereof; or where two R groups are combined as a C_8-C_{30} cycloalkene where the alkylene portion of the cycloalkene is substituted or unsubstituted and/or interrupted one or more times with O, NR', C(O), C(O)O, and/or C(O)NR", where R'

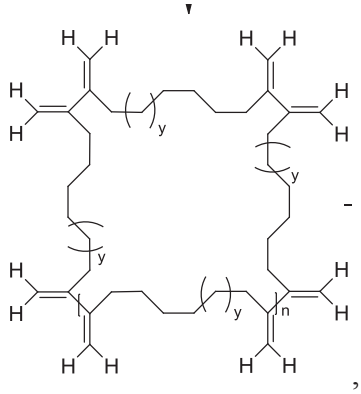
and/or R", when present are each independently H, C_{1-30} alkyl, or C_3 to C_{30} alkenyl. The macrocyclic polyalkene copolymer can have a structure of

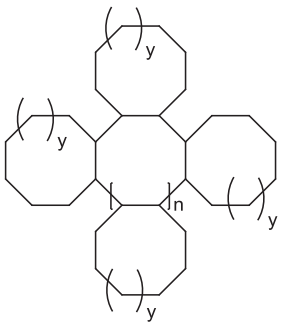


wherein R and R' in the structure are each independently an R as defined in claim 1, and each of n, x, and y is independently an integer of 1 to 100.

[0008] In some cases, provided herein are macrocyclic polyalkanes or macrocyclic poly(alkane-co-alkene)s that include alkane repeating units have the structure -RHC-CHR- and, optionally, alkene repeating units have the structure -RC=CR- or –C(=CR_2)-'s, where, if present, the R of the -RC=CR- alkene repeating units are the same as the R units of at least one of the alkane repeating units. The R groups are independently: H; a substituted or unsubstituted C_1 to C_{30} alkyl, or, when absent an alkene repeating unit or comprising exclusively one unsubstituted alkane repeating units or a copolymer with –H_2C-CH_2- repeating units, R is C_{1-3}, C_5, C_{8-12}, or C_{14-30}; substituted or unsubstituted C_3 to C_{30} alkenyl having one or more alkene bonds where a plurality of alkene bonds can be non-conjugated, conjugated, or a mixture thereof; or where two R groups are combined as a C_8-C_{30} cycloalkane and/or cycloalkene where the alkylene portion of the cycloalkane and/or alkene is substituted or unsubstituted and/or interrupted one or more times with O, NR', C(O), C(O)O, and/or C(O)NR", where R' and/or R", when present, are each independently H, C_{1-30} alkyl, C_3 to C_{30} alkenyl. In examples, the macrocyclic polyalkane or macrocyclic poly(alkane-co-alkene) can have a structure



,


,


or

wherein R and R' in the first structure are each independently an R as defined above, the H atoms depicted in the second structure can be H or another R group as defined above, and each of n, x, and y is an integer of 1 to 100.

[0009] Further provided are methods of forming a macrocyclic polyalkane or a macrocyclic poly(alkane-co-alkene) by reacting a macrocyclic polyalkene and hydrogen in the presence of a hydrogenation catalyst to form the polyalkane or poly(alkane-co-alkene), and isolating the macrocyclic polyalkane or a macrocyclic poly(alkane-co-alkene).

[0010] Also provided are methods of forming a macrocyclic polyalkane or a macrocyclic poly(alkane-co-alkene) by reacting a macrocyclic poly(cycloalkene) with an excess of an alkene and an olefin metathesis catalyst thereby forming a macrocyclic poly(alkane-co-alkene) comprising vicinal $–C(=CR_2)-$ groups, and optionally isolating the macrocyclic polyalkane or the macrocyclic poly(alkane-co-alkene) comprising $–C(=CR_2)-$ groups. The macrocyclic polyalkane or the macrocyclic poly(alkane-co-alkene) comprising $–C(=CR_2)-$ groups can be reacted with hydrogen in the presence of a hydrogenation catalyst thereby forming a macrocyclic polyalkane or a macrocyclic poly(alkane-co-alkene) comprising isolated $–C(C=CR_2)$ groups. The macrocyclic poly(alkane-co-alkene) comprising isolated $–C(=CR_2)-$ groups can react in the presence of an olefin metathesis catalyst to condense isolated $–C(=CR_2)-$ groups intermolecularly into a poly(macrocyclic poly(alkane-co-alkene)) comprising C=C links between macrocyclic poly(alkane-co-alkene). The poly(macrocyclic poly(alkane-co-alkene)) can be hydrogenated to form a poly(macrocyclic poly(alkane)). A dilute solution of the macrocyclic poly(alkane-co-alkene) comprising isolated $–C(=CR_2)-$ groups can be combined with an olefin metathesis catalyst and condensed to form bi-macrocyclic, tri-macrocyclic and/or multi-macrocyclic poly(alkane-co-alkene)s. The bi-macrocyclic, tri-macrocyclic and/or multi-macrocyclic poly(alkane-co-alkene)s can be

hydrogenated to form bi-macrocyclic, tri-macrocyclic and/or multi-macrocyclic poly(alkane)s.

[0011] Further examples and advantages will be apparent to those of ordinary skill in the art from a review of the following detailed description, taken in conjunction with the drawings. The description hereafter includes specific examples with the understanding that the present disclosure is illustrative, and is not intended to limit the present disclosure to the specific examples described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 is a plot of the log of molecular weight versus elution volume for atactic linear and cyclic polypropylene formed from hydrogenation of cyclic poly(propyne) according to an embodiment of the invention.

[0013] FIG. 2 is a plot of log [η] vs log M for atactic linear and cyclic polypropylene, according to an embodiment of the invention, where [η] is the intrinsic viscosity and M is the viscosity-average molar mass.

[0014] FIG. 3 illustrates the synthesis of a catalyst **4**.

DETAILED DISCLOSURE

[0015] Disclosed herein are macrocyclic poly(alkenes), macrocyclic poly(alkenes-co-alkanes), and macrocyclic poly(alkanes).

[0016] Provided are macrocyclic polyalkene copolymers that are conjugated polyalkenes having no chain ends and are in the form of a macrocycle comprising two or more repeating units have the structure -RC=CR-. As used herein, a polymer "having no chain ends" refers to a polymer wherein the initiating monomer/group is linked to the terminating monomer/group. In some cases, the macrocyclic polyalkanes or macrocyclic poly(alkane-co-alkene)s include alkane repeating units have the structure -RHC-CHR- and, optionally, alkene repeating units have the structure -RC=CR- or are pairs of vicinal –C(=CR_2)-'s, where the R of the -RC=CR- alkene repeating units are the same as the R units of at least one of the alkane repeating units.