H2-O-, m = 2-10, and n = 1-5. Preferably, the comonomer of formula (I) is 1,4-butanediol divinyl ether.

Tung, L.H., et al., *Preparation of Polystyrene with Long Chain Branches via Free Radical Polymerization,* J. Polym. Sci., Polym. Chem. Ed., (1981), 19, 2027-39, discloses the use of small amounts of chain-transferring monomers to copolymerize with styrene, free-radically. Of the comonomers examined, vinylbenzylthiol, yielded polystyrene with a branched structure. The branches are disclosed as occurring mainly in the low molecular weight end of the distribution. Vinylbenzylthiol was also found to be an effective agent for the broadening of the molecular weight distribution.

Tung, L.H., *Branching Kinetics in Copolymerization of Styrene with a Chain-Transfer Monomer,* J. Polym. Sci., Polym. Chem. Ed., (1981), 19, 3209-3217, discloses the use of polymerization kinetics to compute the theoretical molecular weight and degree of branching for the polymerization with styrene with a chain transfer monomer (for example, vinylbenzylthiol).

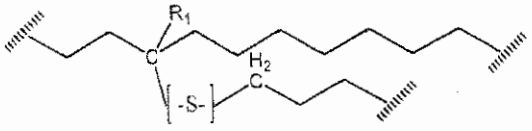
Liu, J., et al., *Branched Polymer via Free Radical Polymerization of Chain Transfer Monomer: A Theoretical and Experimental Investigation*, J. Polym. Sci. Part A: Polym. Chem., (2007), 46, 1449-59, discloses a mathematical model for the free radical polymerization of chain transfer monomers containing both polymerizable vinyl groups and telogen groups. The molecular architecture of the polymer is disclosed as being prognosticated according to the developed model, which was validated experimentally by the homopolymerization of 4-vinyl benzyl thiol (VBT), and its copolymerization with styrene.

However, as discussed, there remains a need for ethylene-based polymers, such as low density polyethylene (LDPE), with improved melt strength, especially for film applications. There is a further need for such polymers with a low insoluble content. These needs and others have been met by the following invention.

SUMMARY ~~OF THE INVENTION~~

The present disclosure~~invention~~ provides an ethylene-based polymer formed from at least the following: ethylene and a "monomeric chain transfer agent (monomeric CTA)," comprising a "copolymerization end" and a "chain transfer end."

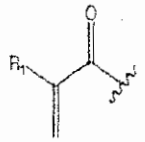
The present disclosure~~invention~~ also provides an ethylene-based polymer comprising at least one structural unit selected from the following:

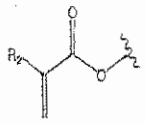


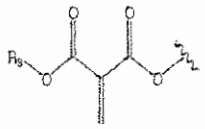
, wherein R1 is selected from H or CH3.

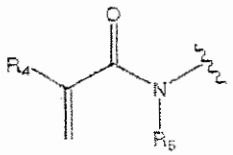
In a first aspect of the present disclosure, there is provided an ethylene-based polymer, comprising a majority amount of polymerized ethylene, based on the weight of the polymer, formed from at least the following: ethylene and a "monomeric chain transfer agent (monomeric CTA)," comprising a "copolymerization end" and a "chain transfer end";

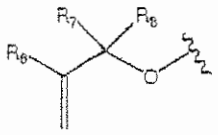
wherein the "copolymerization end" of the monomeric chain transfer agent is selected from the group consisting of the following:

a) , where R1 is selected from H, CH3, CH2CH3, CN, or COCH3;

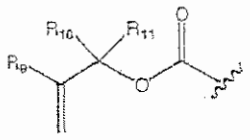
b) , where R2 is selected from H, CH3, CH2CH3, CN, or COCH3;

c) , where R3 is selected from H, C1-C22 alkyl, C3-C8 cycloalkyl, or Phenyl;

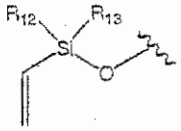
d) , where R4 is selected from H, CH3, CH2CH3, CN, or COCH3, and R5 is selected from H, C1-C22 alkyl, C3-C8 cycloalkyl, Phenyl, or COCH3;

e) 

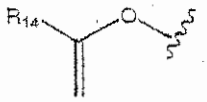
, where R6, R7, R8 are each independently selected from H, CH3 or CH2CH3;

f) 

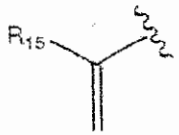
, where R9, R10, R11 are each independently selected from H, CH3, or CH2CH3;

g) 

, where R12, R13 are each independently selected from H, CH3, CH2CH3 or Phenyl;

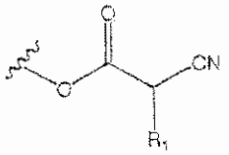
h) 

, where R14 is selected from H, CH3, CH2CH3, or CN; and

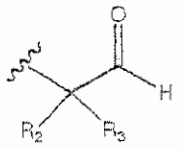
i) 

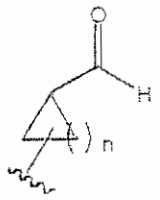
, where R15 is selected from H, C1-C22 alkyl, C3-C8 cycloalkyl or Phenyl, and

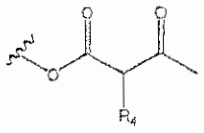
the "chain transfer end" of the monomeric chain transfer agent is selected from the group consisting of the following:

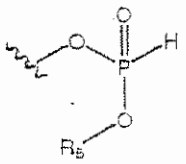
I) 

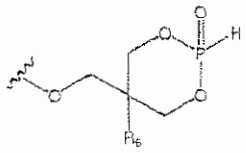
, where R1 is selected from H, C1-C22 alkyl, C3-C8 cycloalkyl, CN, Phenyl, COCH3, CI, Br, or I;

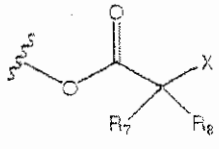
2)  , where R2, R3 are each independently selected from H, C1-C22 alkyl, C3-C8 cycloalkyl, CN, Phenyl, or COCH3;

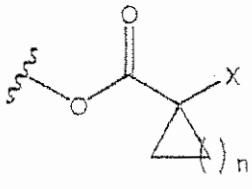
3)  , where n is from 1 to 6;

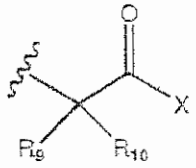
4)  , where R4 is selected from H, C1-C22 alkyl, C3-C8 cycloalkyl, phenyl, Cl, Br, or I;

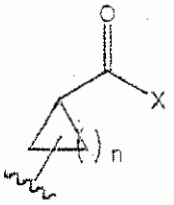
5)  , where R5 is selected from C1-C22 alkyl, C3-C8 cycloalkyl, or Phenyl;

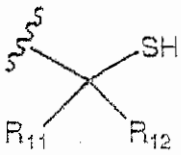
6)  , where R6 is selected from C1-C22 alkyl, C3-C8 cycloalkyl, or Phenyl;

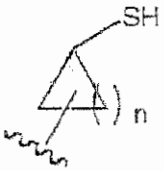
7)  where R7, R8 are each independently selected from H, C1-C22 alkyl, C3-C8 cycloalkyl, Phenyl, Cl, Br, or I; and X is selected from F, Cl, Br, or I;

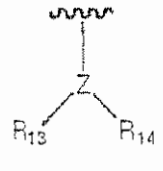
8)  , where X is selected from Cl, Br, or I; and n is from 1 to 6;

9)  , where R9, R10 are each independently selected from H, C1-C22 alkyl, C3-C8 cycloalkyl, CN, Phenyl, or COCH3; and X is selected from Cl, Br, or I;

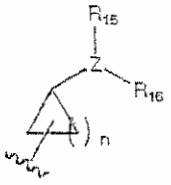
10)  , where X is selected from Cl, Br, or I; and n is from 1 to 6;

11)  , where R11, R12 are each independently selected from H, C1-C22 alkyl, C3-C8 cycloalkyl, CN, Phenyl, or COCH3;

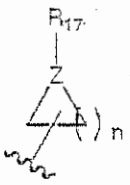
12)  , where n is from 1 to 6;

13) 

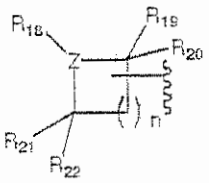
, where R13 is selected from H, C1-C22 alkyl, C3-C8 cycloalkyl, or Phenyl; R14 is selected from H, C1-C22 alkyl, or C3-C8 cycloalkyl; and Z is selected from N or P;

14) 

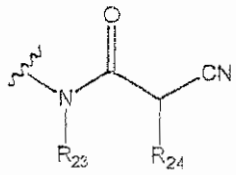
, where R15 is selected from H, C1-C22 alkyl, C3-C8 cycloalkyl, or Phenyl; R16 is selected from H, C1-C22 alkyl, or C3-C8 cycloalkyl; Z is selected from N or P; and n is from 1 to 6;

15) 

, where R17 is selected from H, C1-C22 alkyl, C3-C8 cycloalkyl, or Phenyl; Z is selected from N or P; and n is from 1 to 6;

16) 

, where R18, R19, R20, R21, R22 are each independently selected from H, C1-C22 alkyl, or C3-C8 cycloalkyl; Z is selected from N or P; and n is from 1 to 6; and

17) , where R23 is selected from H, C1-C22 alkyl, C3-C8 cycloalkyl, or Phenyl; and R24 is selected from H, C1-C22 alkyl, C3-C8 cycloalkyl, CN, Phenyl, COCH3, Cl, Br, or I.

In a second aspect of the present disclosure, there is provided a composition comprising the ethylene-based polymer as defined herein.

In a third aspect of the present disclosure, there is provided an article comprising at least one component formed from the composition as defined herein.

BRIEF DESCRIPTION OF THE DRAWINGS

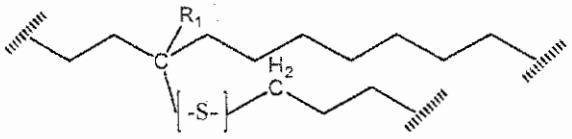
Figure 1 depicts the 1H NMR profile for the control A-0 polymer (lower profile) and the 1H NMR profile for the inventive A-3 polymer (upper profile).

Figure 2 is a plot of extensional viscosity versus time for inventive ethylene-based polymer B-3, at Hencky strain rates of 10 s^{-1}, 1.0 s^{-1} and 0.1 s^{-1}, and at 150°C. In this figure, "Eta*" is the shear viscosity in Pa·s.

DETAILED DESCRIPTION

As discussed above, in a first aspect, the invention provides an ethylene-based polymer formed from at least the following: ethylene and a "monomeric chain transfer agent (monomeric CTA)," comprising a "copolymerization end" and a "chain transfer end."

The invention also provides, in a second aspect, an ethylene-based polymer comprising at least one structural unit selected from the following:

, wherein R1 is selected from H or CH3. Here, the notation "mmmmm" represents a break at the center of a covalent bond between the noted portion of structural unit and a portion of the remaining chemical structure of the polymer.

The following embodiments apply to both the first and second aspects of the invention, except where noted.

In one embodiment, in the first aspect, the "monomeric chain transfer agent" is not a "non-conjugated diunsaturated monomer."

In one embodiment, the ethylene-based polymer comprises, in reacted form, at least 0.075 moles of the monomeric CTA per 1000 moles of ethylene-based polymer backbone carbons, based on the weight of the polymer.

In one embodiment, the ethylene-based polymer comprises, in reacted form, less than, or equal to, 10 moles monomeric CTA per 1000 moles of ethylene-based polymer back bone carbons, based on the weight of the polymer.