PROCESS FOR PREPARING AN OLEFIN-ACRYLATE DIBLOCK COPOLYMER

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims benefit of priority to U.S. Application No. 62/954,941, filed in December 30, 2019, which is incorporated herein by reference in its entirety.

BACKGROUND

[0002] The present disclosure is directed to a process to synthesize olefin-acrylate diblock copolymers using nitroxide-mediated polymerization (NMP) of an acrylate monomer to prepare a functionalized polyacrylate that is subsequently end-capped with an alpha-substituted acrylate monomer (such as an alpha-(alkyl) acrylate monomer or an alpha-(polymeryl) acrylate monomer). During the process, the alpha-substituted acrylate monomer, which is amenable to reaction using standard NMP processes known in the art, is employed as an end-capping monomer of a polyacrylate produced by NMP to form an olefin-acrylate diblock copolymer. This process had not been realized until the disclosures of the present application.

SUMMARY

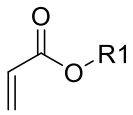
[0003] The present disclosure is directed to a process for preparing an olefin-acrylate diblock copolymer, the process comprising:

a) performing nitroxide-mediated polymerization (NMP) by combining NMP materials comprising an acrylate monomer and a nitroxide initiator, thereby forming a nitroxide macroinitiator; and

b) combining end-capping-reaction materials comprising an alpha-substituted acrylate and the nitroxide macroinitiator, thereby forming the olefin-acrylate diblock copolymer.

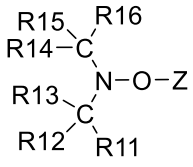
[0003a] In one aspect, there is provided process for preparing an olefin-acrylate diblock copolymer, the process comprising:

a) performing nitroxide-mediated polymerization (NMP) by combining NMP materials comprising an acrylate monomer that has the formula (III):

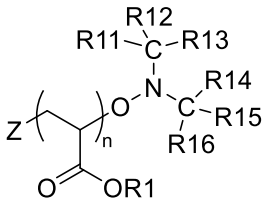


(III)

and a nitroxide initiator that has the formula (IV):

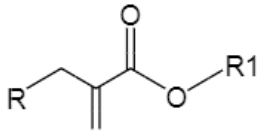


(IV), thereby forming a nitroxide macroinitiator that has the formula (V):



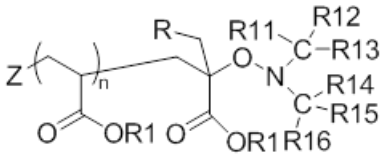
(V); and

b) combining end-capping-reaction materials comprising an alpha-substituted acrylate that has the formula (II):



(II)

and the nitroxide macroinitiator, thereby forming the olefin-acrylate diblock copolymer that has the formula (VI):



(VI);

wherein each R1 independently is a C1-C30 hydrocarbyl group and each R independently is a C1-C26 hydrocarbyl group, and each Z independently represents a group having at least one carbon atom and is such that the free radical Z· derived from Z is is capable of initiating polymerization of the acrylate monomer of the formula (III) by free radical polymerization and the radical functionality resides in a carbon atom;

each R16, R15, R12, and R11 represent the same or different straight chain or branched substituted or unsubstituted alkyl groups of a chain length sufficient to provide steric hindrance and weakening of the O—Z bond of the compound of the formula (IV);

each R14 and R13 represent the same or different straight chain or branched substituted alkyl groups or R14CNCR13 may be part of a cyclic structure which may have fused with it another saturated or aromatic ring, the cyclic structure or aromatic ring being optionally substituted; and n is from 2 to 500.

BRIEF DESCRIPTION OF DRAWINGS

[0004] FIGS. 1A and 1B provide the 1H NMR and 13C NMR spectra, respectively, for Example 1.

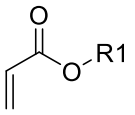
DETAILED DESCRIPTION

Definitions

[0005] All references to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 2003. Also, any references to a Group or Groups shall be to the Group or Groups reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups.

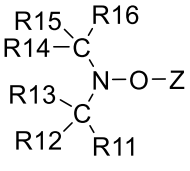
Claims:

1. A process for preparing an olefin-acrylate diblock copolymer, the process comprising:
   a) performing nitroxide-mediated polymerization (NMP) by combining NMP materials comprising an acrylate monomer that has the formula (III):

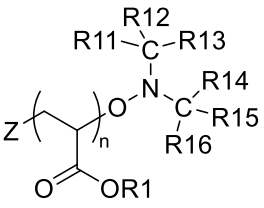


(III)

and a nitroxide initiator that has the formula (IV):

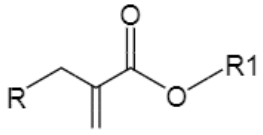


(IV), thereby forming a nitroxide macroinitiator that has the formula (V):



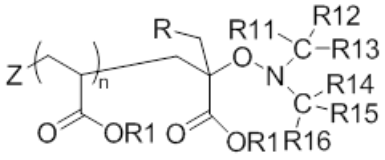
(V); and

   b) combining end-capping-reaction materials comprising an alpha-substituted acrylate that has the formula (II):



(II)

and the nitroxide macroinitiator, thereby forming the olefin-acrylate diblock copolymer that has the formula (VI):



(VI);

wherein each R1 independently is a C1-C30 hydrocarbyl group and each R independently is a C1-C26 hydrocarbyl group, and each Z independently represents a group having at least one carbon atom and is such that the free radical Z· derived from Z is is capable of initiating polymerization of the acrylate monomer of the formula (III) by free radical polymerization and the radical functionality resides in a carbon atom;

each R16, R15, R12, and R11 represent the same or different straight chain or branched substituted or unsubstituted alkyl groups of a chain length sufficient to provide steric hindrance and weakening of the O—Z bond of the compound of the formula (IV);

each R14 and R13 represent the same or different straight chain or branched substituted alkyl groups or R14CNCR13 may be part of a cyclic structure which may have fused with it another saturated or aromatic ring, the cyclic structure or aromatic ring being optionally substituted; and n is from 2 to 500.

2. The process of claim 1, wherein each R independently is a C1-C26, C1-C10, or C1-C8 alkyl group that is linear, branched, or cyclic.

3. The process of claim 1 or 2, wherein each of steps a) and b) is performed at a temperature from 100°C to 150°C.