SUMMARY

[0004] This disclosure accordingly provides systems and methods for monitoring and controlling a nitroxide-based polymerization inhibitor in vinyl-based monomers, substantially in real time. The online monitoring of nitroxide-based inhibitor concentration can be correlated to an extent of undesirable polymerization. Moreover, the online monitoring of nitroxide-based inhibitor concentration can be used as an indirect probe of additional factors affecting the overall polymerization kinetics, such as the dosage of secondary slower-acting polymerization retarders or antioxidants.

[0005] In an aspect, the present disclosure provides a method of monitoring and controlling a nitroxide-based polymerization inhibitor in vinyl-based monomers. The method includes providing a dosage of the nitroxide-based polymerization inhibitor in the vinyl-based monomers. The vinyl-based monomers are conditioned in a fast flow sampling loop. A residual concentration of the nitroxide-based polymerization inhibitor is measured after the fast flow sampling loop substantially in real time, and an optimized dosage of the nitroxide-based polymerization inhibitor is provided in response to the measured residual concentration.

[0006] In another aspect, the present disclosure provides a system for monitoring and controlling undesirable polymerization in vinyl-based monomers. The system includes a fast flow sampling loop, wherein the fast flow sampling loop is configured to condition the vinyl-based monomers before flowing the conditioned vinyl-based monomers to a control module, and ~~a~~ the control module connected to the fast flow sampling loop. The control module is capable of controlling sample conditioning and measuring a residual concentration of a nitroxide-based polymerization inhibitor in the conditioned vinyl-based monomers substantially in real time.

[0007] The foregoing has outlined rather broadly the features and technical advantages of the present disclosure in order that the detailed description of the present disclosure that follows may be better understood. Additional features and advantages of the present disclosure will be described hereinafter that form the subject of the claims of the present disclosure. It should be appreciated by those skilled in the art that the conception and the specific embodiments disclosed may be readily utilized as a basis for modifying or designing other embodiments for carrying out the same purposes of the present disclosure. It should also be realized by those skilled in the art that such equivalent embodiments do not depart from the spirit and scope of the present disclosure as set forth in the appended claims.

CLAIMS

What is claimed is:

1. A method of monitoring and controlling a nitroxide-based polymerization inhibitor in vinyl-based monomers, the method comprising:

providing a dosage of the nitroxide-based polymerization inhibitor in the vinyl-based monomers;

conditioning the vinyl-based monomers in a fast flow sampling loop;

measuring a residual concentration of the nitroxide-based polymerization inhibitor after the fast flow sampling loop substantially in real time; and

providing an optimized dosage of the nitroxide-based polymerization inhibitor in response to the measured residual concentration.

2. The method of claim 1, wherein the residual concentration is measured on a substantially continuous basis.

~~3. The method of claim 1 further comprising providing a fast flow sampling loop, and wherein the residual concentration of the nitroxide-based inhibitor is measured after the fast flow sampling loop.~~

~~4.~~3. The method of claim ~~3~~1, wherein after the fast flow sampling loop resides a continuous stirred tank reactor and an apparatus for providing the optimized dosage of the nitroxide-based inhibitor into the continuous stirred tank reactor and wherein the residual concentration of the nitroxide-based inhibitor is measured from the contents of the continuous stirred tank reactor.

~~5.~~4. The method of claim 1 further comprising evaluating a degree of undesirable polymerization in the vinyl-based monomer based on the measured residual concentration.

~~6.~~5. The method of claim ~~5~~4, wherein the degree of undesirable polymerization is evaluated using at least one of an electron spin resonance spectrometer, a gas chromatograph, a gas chromatograph-mass spectrometer, liquid chromatography, nuclear magnetic resonance, x-ray diffraction, x-ray fluorescence, atomic absorption, inductively coupled plasma emission spectroscopy, an ultraviolet-visible spectrometer, an infrared spectrometer, a near-infrared spectrometer, a Raman spectrometer, a fluorometer, a turbidimeter, dynamic light scattering, evaporative light scattering, and a titrator.

~~7.~~6. The method of claim ~~5~~4 further comprising co-dosing one or more retarders and/or antioxidants to the vinyl-based monomers and evaluating an effect of the co-dosed retarders and/or antioxidants on the degree of undesirable polymerization based on the measured residual concentration.

7. The method of claim 6, wherein an optimized dosage of the co-dosed retarders and/or antioxidants is also provided in response to the measured residual concentration.

8. The method of claim 6 or 7, wherein the effect of the co-dosed retarders and/or the antioxidants is evaluated using at least one of an electron spin resonance spectrometer, a gas chromatograph, a gas chromatograph-mass spectrometer, liquid chromatography, nuclear magnetic resonance, x-ray diffraction, x-ray fluorescence, atomic absorption, inductively coupled plasma emission spectroscopy, an ultraviolet-visible spectrometer, an infrared spectrometer, a near-infrared spectrometer, a Raman spectrometer, a fluorometer, a turbidimeter, dynamic light scattering, evaporative light scattering, and a titrator.

9. The method of any one of claims 6-8, wherein at least one of the co-dosed retarders is non-nitroxide-based.

10. The method of any one of the preceding claims ~~1~~, wherein the optimized dosage is so determined as to control an undesirable polymerization of the vinyl-based monomer during manufacture and purification thereof.

11. The method of claim 1, wherein the nitroxide-based polymerization inhibitor includes 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl.

12. The method of claim 1, wherein the measured residual concentration is about 1 ppb to about 10,000 ppm.

13. A system for monitoring and controlling undesirable polymerization in vinyl-based monomers, comprising:

a fast flow sampling loop, wherein the fast flow sampling loop is configured to condition the vinyl-based monomers before flowing the conditioned vinyl-based monomers to a control module; and

a the control module connected to the fast flow sampling loop, the control module being capable of controlling sample conditioning and measuring a residual concentration of a nitroxide-based polymerization inhibitor in the conditioned vinyl-based monomers substantially in real time.

14. The system of claim 13, wherein after the fast flow sampling loop resides a continuous stirred tank reactor, and wherein the control module is capable of measuring the residual concentration of the nitroxide-based inhibitor in the continuous stirred tank reactor.

15. The system of claim 13 further comprising a nitroxide-based polymerization inhibitor dosing pump that is connected to the control module, wherein the control module selectively activates the nitroxide-based polymerization inhibitor dosing pump so as to control the undesirable polymerization of the vinyl-based monomers during manufacture and purification thereof.

16. The system of claim 13 further comprising a non-nitroxide-based retarder dosing pump.

17. The system of claim 13, wherein the nitroxide-based polymerization inhibitor includes 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl.

18. The system of claim 13, wherein the fast flow sampling loop is configured to obtain a sample slipstream comprising the vinyl-based monomers and to condition the sample slipstream before flowing the conditioned sample slipstream to the control module.

19. The system of claim 18 further comprising a check valve that facilitates moving the sample slipstream toward a predetermined direction.

20. The system of claim 13, wherein the measured residual concentration is about 1 ppb to about 10,000 ppm.