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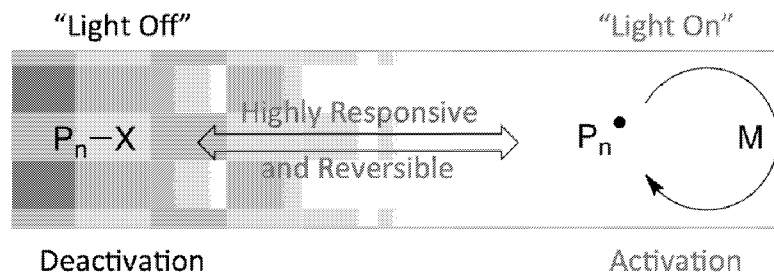
FIG. 1

(57) **Abstract**: Living radical polymerization processes have emerged as one of the most powerful synthetic strategies for the preparation of a wide variety of functional materials. The ability to regulate these processes with an external stimulus dramatically increases their utility and further allows living radical polymerization processes to provide new macromolecular structures and facilitate an even greater range of applications. This application discloses a living radical polymerization procedure that provides control over chain growth through mediation by visible light. Embodiments of the invention show an unprecedented activation and deactivation of polymerization reactions by visible light as well as an excellent control over the molecular weight and molecular weight distributions of polymers formed by this method.

CONTROL OF LIVING RADICAL POLYMERIZATION BY LIGHT

REFERENCE TO RELATED APPLICATIONS

This application claims the benefit under 35 U.S.C. Section 119(e) of co-
5   pending U.S. Provisional Patent Application Serial No. 61/615,458, filed on March
26, 2012, entitled "CONTROL OF LIVING RADICAL POLYMERIZATION BY
LIGHT" the contents of which are incorporated herein by reference. This application
is related to co-pending U.S. Provisional Patent Application Serial No. 61/711,920,
filed on October 10, 2012, entitled "SPATIAL AND TEMPORAL CONTROL OF
10   BRUSH FORMATION ON SURFACES" the contents of which are incorporated
herein by reference.

TECHNICAL FIELD

The invention relates to controlled radical polymerizations utilizing
15   photoredox catalyst that are mediated, as well as regulated, by light.

BACKGROUND OF THE INVENTION

The ability to precisely control the molecular weight and molecular weight
distributions, as well as gain sequence and architecture control in polymer synthesis is
20   of considerable importance in a variety of technologies. For example, the
development of controlled polymerization methods has profoundly changed polymer
research with strategies, such as nitroxide-mediated radical polymerization (NMP),
atom transfer radical polymerization (ATRP), and reversible addition fragmentation
chain transfer polymerization (RAFT), processes that allow the facile synthesis of
25   well-defined polymers that are diverse in both their structure and function (see, e.g. C.
J. Hawker, et al. *Chem. Rev.* 2001, 101, 3661 – 3688).

Understandably, there have been a number of efforts to increase the technical
applicability of polymerization processes, for example through strategies to regulate
the activation and deactivation steps by using an external stimulus. However, there

are few descriptions in the art of this type of regulation being successfully achieved through redox-controlled processes, electrochemical techniques, mechanochemical methods, or the allosteric control of catalysis. One strategy that controls both the initiation and growth exploits the unique aspects of electrochemistry to control the ratio of activator to deactivator in ATRP (see, e.g. A. J. D. Magenau, et al. *Science* 2011, 332, 81 – 84). With the selective targeting of redox-active catalytic species, this polymerization reaction can be turned "on" and "off" by adjusting parameters such as applied current, potential, and total charge passed. However, all of the conventional approaches in this technology are limited by the complexity of the systems, the use of specialized monomers, the requirement of restrictive equipment and/or a lack of responsive dynamic control.

As with traditional radical polymerization, the most robust and widely used form of regulation is through photo-polymerization. Unfortunately however, the most useful form of external stimuli, light irradiation, has not been successfully used in ATRP reactions (see, e.g. M. Tanabe, et al. *Nat Mater* 2006, 5, 467 – 470; Y. Kwak, et al. *Macromolecules* 2010, 43, 5180 – 5183). While some photoinitiatable ATRP reactions have been developed, in these studies, only the initiation step was photocontrolled. Consequently, all subsequent growth steps in such reactions could not be photoregulated. Moreover, attempts to develop polymerization processes that are controllable by UV irradiation have been hampered by poor control and broad molecular weight distributions (see, e.g. T. Otsu, et al. *Makromol. Chem. Rapid Commun.* 1982, 3, 127 – 132).

An ability to adapt new polymerization processes to the large number of technologies that utilize polymers is highly desirable. For this reason, the development of a photo-controlled radical polymerization process represents a significant breakthrough in this technical field.

SUMMARY OF THE INVENTION

The invention disclosed herein involves a radical polymerization process that is easily and precisely controllable via light. The characteristics of this polymerization process make it a versatile platform for the preparation of a wide variety of functional materials that can be adapted for use in a number of contexts. As discussed in detail below, the invention disclosed herein has a number of embodiments that include methods, materials and systems for making and using polymers formed by these photo-controlled polymerization processes. The polymer compositions of the invention include a variety of polymeric structures including for example, block copolymers and the like.

The invention disclosed herein has a number of embodiments. Illustrative embodiments of the invention include compositions of matter comprising a plurality of polymer chains, wherein the polymer chains undergo a radical polymerization process that is reversibly activated in the presence of light and reversibly deactivated in the absence of light. In such embodiments, the composition typically comprises monomers that form the polymer chains in the radical polymerization process, an initiator that reacts with the monomers in the radical polymerization process to form an intermediate compound capable of linking successively with the monomers to form the polymer chains, and a photoredox catalyst. As discussed in detail below, the relative amounts of the reagents used to form these polymers can be controlled in order to control one or more aspects of the polymer molecules such as the polydispersity of the polymer chains. For example, in typical embodiments of the invention, a reagent such as the initiator or the photoredox catalyst is present in the composition in a sub-stoichiometric amount. Optionally, for example, the amount of catalyst is less than 20 mol % but more than 0.00001 mol % relative to the amount of monomer used.

Illustrative embodiments of the invention include methods for making polymers using a photo-controlled radical polymerization process. An illustrative embodiment is a method of forming polymer chains that are capable of undergoing a

radical polymerization process that is reversibly activated in the presence of light and reversibly deactivated in the absence of light. This method comprises the steps of combining together a reaction mixture comprising monomers that can form the polymer chain subunits in a radical polymerization process, an initiator that reacts

5   with monomers in the radical polymerization process to form an intermediate compound capable of linking successively with the monomers to form the polymer chains, and a photoredox catalyst. The reagents used in these methods are selected so that exposing this reaction mixture to light initiates a reversible and photo-controlled radical polymerization process, one that produces polymer chains characterized by

10   their ability to reversibly activate chain growth in the presence of light and reversibly deactivate chain growth in the absence of light.

In some embodiments of the invention, a property of the polymer chains (e.g. chain length, chain molecular weight distributions or chain architecture) is controlled by controlling the relative amounts of reagents used in the reaction mixture and/or by

15   controlling an amount of time that compounds the reaction mixture are exposed to light; and/or controlling an intensity of light that reaches the reaction mixture. Optionally, the method comprises exposing a reaction mixture to light so that the polymer chains exposed to light exhibit a polydispersity such that M_w/M_n is between 1.0 and 2.0, wherein M_w = the weight average molecular weight of the plurality of

20   polymer chains; and M_n = the number average molecular weight of the plurality of polymer chains.

Yet another embodiment of the invention is a polymerization system comprising monomers that form polymer chain subunits in a radical polymerization process, an initiator that reacts with monomers in the radical polymerization process

25   to form an intermediate compound capable of linking successively with the monomers to form the polymer chains, and a photoredox catalyst. In this system, the reagents and reaction conditions are selected so that monomers, initiator and catalyst combined in a reaction mixture will form a plurality of polymer chains that undergo a radical polymerization process that is reversibly activated in the presence of light and

reversibly deactivated in the absence of light. In certain embodiments, the polymerization system includes a solvent in which the monomers, initiator and catalyst can be combined in the reaction mixture and/or a reaction vessel in which the monomers, initiator and catalyst can be combined so as to form the plurality of polymer chains and/or a light source, wherein the amount and/or intensity of light produced by the light source is controllable and/or a filter that modulates the intensity of the light from the light source.

Optionally, the polymerization system is in the form of a kit, for example one including a plurality of containers that hold the reagents used to form the polymers. In one illustrative embodiment, the kit includes one or more reagents used to form polymers (e.g. initiators, monomers, catalysts, solvents and the like) as well as articles useful to control polymer growth, for example a controllable light source, one or more light filters and the like.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1: diagram showing aspects of a polymerization scheme that allows, for example, temporal and spatial control over radical polymerization reactions using light.

Figure 2: graphs showing the polymerization of MMA using catalyst 1 while cycling the reaction's exposure to visible light. (A) Conversion vs. time; (B) time of light exposure vs. $\ln([M]_0/[M]_t)$, with $[M]_0$ and $[M]_t$ being the concentrations of monomers at time points zero and t, respectively; (C) conversion vs. M_n ($\bullet$) and conversion vs. M_w/M_n (Δ).

Figure 3: diagram showing synthesis of a poly(methyl methacrylate)-*b*-(benzyl methacrylate) diblock copolymer. (B) graphed data from a size exclusion chromatogram with the gray and black traces corresponding to 4 and 3, respectively.

Figure 4: a schematic of a proposed mechanism of a visible-light-mediated radical polymerization using an Ir-based photoredox catalyst. P_n=polymer chain.

Figure 5: a schematic and Table showing data on molecular weight and polydispersities for the visible-light-mediated polymerization of methyl methacrylate using [Ir(ppy)₃].

Figure 6: a schematic and Table showing data on the synthesis of random copolymers and the homopolymer of methacrylic acid (MAA).

Figure 7: photographic image of illustrative equipment used in polymerization reactions.

Figure 8: graphed data showing fluorescence of a 0.13 mM solution of 1 in DMF with varying concentrations of methyl methacrylate (MMA) or ethyl α-bromophenylacetate (initiator).

Figure 9: graphed data showing fluorescence of a 0.13 mM solution of 1 in DMF with varying concentrations of methyl methacrylate (MMA).

Figure 10: graphed data showing fluorescence of a 0.13 mM solution of 1 in DMF with varying concentrations of ethyl α-bromophenylacetate (initiator).

Figure 11: graphed data showing conversion vs time for the polymerization of methyl methacrylate.

Figure 12: graphed data showing conversion vs number average molecular weight (circle) and conversion vs the molecular weight distribution (triangle) for the polymerization of methyl methacrylate.

Figure 13: drawings of illustrative initiators that can be used in embodiments of the invention.

Figure 14A-C: show drawings of illustrative photoredox catalysts that can be used in embodiments of the invention, while **Figure 14D-F**: show drawings of illustrative ligands that can be used in embodiments of the invention.

DETAILED DESCRIPTION OF THE INVENTION

Unless otherwise defined, all terms of art, notations and other scientific terms or terminology used herein are intended to have the meanings commonly understood by those of skill in the art to which this invention pertains. In the description of

illustrative embodiments, reference is made to the accompanying drawings which form a part hereof, and in which is shown by way of illustration a specific embodiment in which the invention may be practiced. It is to be understood that other embodiments may be utilized and structural changes may be made without departing

5   from the scope of the present invention.

A new controlled radical polymerization which is adapted for controlled polymer formation and which displays an unprecedented response to activation and deactivation of polymerization through external visible light stimulation is disclosed herein. The advantages of this approach lie in its highly responsive nature, facile

10   reaction setup, use of only ppm levels of catalyst, and excellent functional group tolerance. In analogy with the pervasive nature of traditional photopolymerization and ATRP procedures, this photocontrolled radical polymerization offers a versatile platform for the preparation of functional materials with applications in sustainability, electronics, and health. A number of illustrative and working embodiments of the

15   invention and/or methods and materials that can be used with embodiments of the invention are discussed below.

The invention disclosed herein has a number of embodiments that include methods, materials and systems for making and using polymers using a photo-controlled radical polymerization process. Illustrative embodiments of the invention

20   include methods of forming polymers using a photo-controlled radical polymerization process that is reversibly activated in the presence of light and reversibly deactivated in the absence of light. Significantly, this photo-controlled radical polymerization process can be activated and/or deactivated multiple times simply by exposing the polymerization reactants to light and/or shielding the polymerization reactants from

25   light. In this context, while a small amount of polymer chain termination may be occurring in these radical polymerization processes, they nonetheless exhibit characteristics of a "living polymerization process" (i.e. an addition polymerization processes where the ability of a growing polymer chain to terminate has been removed). Controlled and living polymerization processes are known in the art and

described, for example, in A. H. E. Müller, K. Matyjaszewski, *Controlled and Living Polymerizations*: Methods and Materials, Wiley-VCH, Weinheim, 2009.

Typically, a polymerization process of the invention comprises the steps of forming a plurality of polymer chains by forming a reaction mixture that includes the

5   monomers that form polymer chain subunits in the radical polymerization process, an initiator that reacts with the monomers in the radical polymerization process to form an intermediate compound capable of linking successively with the monomers to form the polymer chains, and a photoredox catalyst. In this process, the reagents are selected so that the polymer chains undergo a radical polymerization process that is

10   reversibly activated in the presence of light and reversibly deactivated in the absence of light. Moreover, reagent use can be controlled in these methods so that, for example, a reagent such as the initiator or photoredox catalyst is present in the reaction mixture in sub-stoichiometric amounts and serves as a process limiting reagent. In this context, when the reaction mixture is exposed to light, the radical

15   polymerization process is initiated in the light exposed areas so that polymers are formed.

Methods of the invention allow precise control of polymer growth so as to form polymers having selected lengths and/or selected molecular weights (e.g. within selected mw ranges) and/or selected molecular weight distributions and/or selected

20   architectures. In certain embodiments of the invention, polymer chains are formed to have a structure selected from a group consisting of block copolymers; random copolymers; gradient copolymers; periodic polymers; alternating polymers; statistical polymers; linear polymers; branched polymers; star polymers; brush polymers; comb polymers; and graft polymers.

25   As the rate of polymer formation is shown to be directly proportional to the amount of light exposure in embodiments of the disclosed processes, optionally, for example, polymer chain lengths in a reaction mixture are controlled by controlling an amount of time that the reaction mixture is exposed to light; and/or by controlling an intensity of light that reaches the reaction mixture. Embodiments of the invention can

comprise exposing a reaction mixture to light multiple times in order to precisely tailor one or more characteristics of a polymer composition. For example, in some methods of the invention, a reaction mixture is first exposed to light for a period of time so that the radical polymerization process is activated; followed by a step in which this reaction mixture is protected from light exposure for a period of time so that the radical polymerization process is deactivated; and then re-exposing the reaction mixture to light for a period of time so that the radical polymerization process is re-activated etc.

The methods disclosed herein can be used to form polymeric materials that have a number of desirable qualities including for example, a relatively low polydispersity. As is known in the art, the polydispersity index (PDI) is a measure of the distribution of molecular mass in a given polymer sample. The PDI calculated is the weight average molecular weight (Mw) divided by the number average molecular weight (Mn). The index indicates the distribution of individual molecular masses in a batch of polymers. The PDI from polymerization is often denoted as: PDI = Mw/Mn, where Mw is the weight average molecular weight and Mn is the number average molecular weight. Optionally in embodiments of the invention, polymer chain growth is controlled so that the polymer chains in a reaction mixture that are exposed to a specific amount of light (e.g. a specific frequency of light and/or a specific wavelength of light and/or light having a specific photon energy level and/or a specific power of light) exhibit a polydispersity index such that M_w/M_n is between 1.0 and 2.0 (e.g. 1.05 and 1.5). In certain embodiments of the invention, different portions of regions of a reaction mixture are exposed to different amounts of light and, when examined in aggregate, the polydispersity index of the polymer chains is greater than 2.0, and can be, for example, greater than 5, 10, 25, 50, 100, 150 or 200.

One embodiment of the invention is a composition comprising a plurality of polymer chains that undergo a radical polymerization process that is reversibly activated in the presence of light and reversibly deactivated in the absence of light. In this embodiment, the reagents of the composition allow the polymer chains to

undergo a radical polymerization process that is reversibly activated in the presence of light and reversibly deactivated in the absence of light. As this process is reversibly activated in the presence of light and reversibly deactivated in the absence of light, a polymerization process can be initiated and/or deactivated multiple times simply by exposing the polymerization reactions to light and/or shielding the polymerization reactions from light. The methods of the invention can be used to form a variety of compositions having various polymeric structures including for example, block copolymers, random copolymers; gradient copolymers; periodic polymers; alternating polymers; statistical polymers; linear polymers; branched polymers; star polymers; brush polymers; comb polymers; graft polymers and the like.

The invention disclosed herein has a number of embodiments. Illustrative embodiments of the invention include compositions of matter comprising a plurality of polymer chains, wherein the polymer chains undergo a radical polymerization process that is reversibly activated in the presence of light and reversibly deactivated in the absence of light. In such embodiments, the composition typically comprises monomers that form the polymer chains in the radical polymerization process, an initiator that reacts with the monomers in the radical polymerization process to form an intermediate compound capable of linking successively with the monomers to form the polymer chains, and a photoredox catalyst. As discussed in detail below, the relative amounts of the reagents used to form these polymers can be controlled in order to control one or more aspects of the polymer molecules such as the polydispersity of the polymer chains. For example, in some embodiments, a reagent such as the initiator or the photoredox catalyst is present in the composition in a sub-stoichiometric amount. In certain methodological embodiments of the invention, the amount of initiator added to a reaction mixture is controlled to control the molecular weight of the final polymer product. In some embodiments, the amount of catalyst is less than 20 mol % but more than 0.00001 mol % relative to the amount of monomer used.

As discussed in detail below, a variety of different monomers, initiators, catalysts and other reagents such as solvents can be used to make embodiments of the invention. In some embodiments of the invention, the monomers comprise an alkene moiety. Optionally, the monomer comprises an acrylate, a methacrylate, a styrene, a

5   vinyl acetate, a vinylpyridine or a vinyl chloride. In some embodiments of the invention, the initiator comprises a halide or a pseudo halide. In certain embodiments of the invention, the initiator comprises a xanthate, a thioesters, a thionoester, a dithioesters, a trithioesters or a nitroxide. Typically, the catalyst comprises a transition metal photoredox catalyst having a transition metal selected from the group

10   consisting of Ir, Co, Fe, Rh, Pt, Pd, Mn, Os, Eu, Cr, Cu, Al, Ti, Zn, Cd and Ru.

In typical embodiments, the polymer chains in a polymer composition (e.g. those exposed to a specific amount of light) exhibit a polydispersity resulting from light exposure wherein M_w/M_n is between 1.0 and 2.0, wherein M_w = the weight average molecular weight of the plurality of polymer chains; and M_n = the number

15   average molecular weight of the plurality of polymer chains. Embodiments of the invention include forming macromolecular structures by cross-linking the polymer compositions.

Illustrative embodiments of the invention include methods for making polymers using a photo-controlled radical polymerization process. An illustrative

20   embodiment is a method of forming polymer chains that are capable of undergoing a radical polymerization process that is reversibly activated in the presence of light and reversibly deactivated in the absence of light. This method comprises the steps of combining together a reaction mixture comprising monomers that can form the polymer chain subunits in a radical polymerization process, an initiator that reacts

25   with monomers in the radical polymerization process to form an intermediate compound capable of linking successively with the monomers to form the polymer chains, and a photoredox catalyst. The reagents used in these methods are selected so that exposing this reaction mixture to light initiates a reversible and photo-controlled radical polymerization process, one that produces polymer chains characterized by

their ability to reversibly activate chain growth in the presence of light and reversibly deactivate chain growth in the absence of light.

Certain embodiments of the invention can include multiple polymerization activation and deactivation steps. For example, in some embodiments of the invention, the method comprises the sequential steps of exposing compounds combined in a reaction mixture to light for a period of time so that the radical polymerization process is activated and then protecting this reaction mixture from light exposure for a period of time so that the radical polymerization process is deactivated, and then re-exposing this reaction mixture to light for a period of time so that the radical polymerization process is re-activated etc. etc.

In some embodiments of the invention, a property of the polymer chains (e.g. chain length, chain molecular weight distributions or chain architecture) is controlled by controlling the relative amounts of reagents used in the reaction mixture and/or by controlling an amount of time that compounds the reaction mixture are exposed to light; and/or controlling an intensity of light that reaches the reaction mixture. Optionally, the method comprises exposing a reaction mixture in to light so that the polymer chains exposed to light exhibit a polydispersity such that M_w/M_n is between 1.0 and 2.0, wherein M_w = the weight average molecular weight of the plurality of polymer chains; and M_n = the number average molecular weight of the plurality of polymer chains.

Yet another embodiment of the invention is a polymerization system comprising monomers that form polymer chain subunits in a radical polymerization process, an initiator that reacts with monomers in the radical polymerization process to form an intermediate compound capable of linking successively with the monomers to form the polymer chains, and a photoredox catalyst. In this system, the reagents and reaction conditions are selected so that monomers, initiator and catalyst combined in a reaction mixture will form a plurality of polymer chains that undergo a radical polymerization process that is reversibly activated in the presence of light and reversibly deactivated in the absence of light. In certain embodiments, the

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polymerization system includes a solvent in which the monomers, initiator and catalyst can be combined in the reaction mixture and/or a reaction vessel in which the monomers, initiator and catalyst can be combined so as to form the plurality of polymer chains and/or a light source, wherein the amount and/or intensity of light

5   produced by the light source is controllable and/or a filter that modulates the intensity of the light from the light source.

Embodiments of the invention also provide articles of manufacture and kits for forming the disclosed polymers. In one illustrative embodiment, the kit includes one or more reagents used to form the disclosed polymers (e.g. monomers, initiators,

10   catalysts, solvents and the like) as well as articles useful to control polymer growth, for example a controllable light source, one or more light filters and the like. Optionally, the polymerization system is in the form of a kit, for example one including a plurality of containers that hold the reagents used to form the polymers. In one illustrative embodiment, the kit includes one or more reagents used to form

15   polymers (e.g. initiators, monomers, catalysts, solvents and the like) as well as articles useful to control polymer growth, for example a controllable light source, one or more light filters and the like.

ILLUSTRATIVE REAGENTS USEFUL WITH EMBODIMENTS OF THE
20   INVENTION

As is known in the art, polymerization reagents can be selected to modulate aspects of these polymerization reactions. These include monomers, initiators, catalysts, and solvents. Reactions with these compounds can then be carried out on a variety of vessels, for example those of the type shown in Figure 7. Moreover, such

25   reactions are typically carried out in a solvent. As is known in the art, the solvent component of a solution is present in the greatest amount and is the substance in which the solutes are dissolved. Embodiments of the invention can be adapted for use with a variety of solvents known in the art, for example dimethyl formamide (DMF), toluene, 1,4-dioxane, xylene, anisole, DMSO, Tetrahydrofuran (THF), water,

methanol, acetonitrile, chloroform and the like. In addition, in some embodiments of the invention, one or more reactants in the polymerization process (e.g. a monomer) functions as a solvent. In certain working embodiments of the invention, the amounts of monomer present in the reaction mix are greater than the amounts of DMF present

5   in the reaction mix.

As discussed above, an initiator reacts with the monomers in a radical polymerization process to form an intermediate compound capable of linking successively with the monomers to form the polymer chains. In this context, the number of growing polymer chains can be determined by the initiator. The faster the

10   initiation, the fewer terminations and transfers, the more consistent the number of propagating chains leading to narrow molecular weight distributions.

Organic halides can be used as initiators in processes of the invention. Initators for in common embodiments of the invention typically comprise alkyl halides or pseudo halides. Alkyl halides such as alkyl bromides are more reactive

15   than alkyl chlorides. In some embodiments of the invention, the shape or structure of an initiator can be selected to influence the architecture of a polymer. For example, initiators with multiple alkyl halide groups on a single core can lead to a star-like polymer shape. Initiators other than alkyl halide or pseudo halide that can be used in embodiments of the invention include, but are not limited to, xanthates, thioesters,

20   thionoesters, dithioesters, trithioesters, and nitroxides. Illustrative initiators other than ethyl α-bromophenylacetate that can be used in embodiments of the invention include but are not limited to those shown in Figure 13.

As is known in the art, monomers encompass a class of compounds, mostly organic, that can react with other molecules of the same or other compound to form

25   very large molecules, or polymers. Monomers that are typically used in polymerization reactions include molecules with substituents that can stabilize the propagating radicals; for example, styrenes, (meth)acrylates, (meth)acrylamides, and acrylonitrile. Embodiments of the invention can be used to form polymers of high number average molecular weight and a narrow polydispersity index when the

concentration of the propagating radical balances the rate of radical termination. Monomers that undergo radical polymerization in the disclosed process include but are not limited to typical alkene monomers that undergo traditional radical polymerization, such as but not limited to, methyl methacrylate, styrenes, acrylates, methyl acrylate, acrylonitrile, vinyl acetate, vinylpyridine, methacrylic acid, tert-butyl methacrylate, benzyl methacrylate, tert-butyl acrylate, benzyl acrylate, vinyl chloride, acrylamides, acrylic acid. Reactive functional groups on monomers include, but are not limited to, carboxylic acids, epoxides, amines, amides, alcohols, ketones, aldehydes, alkynes, alkenes, fluorides, chlorides, bromides, iodides, ethers, esters, hyroxylamines, imines, azides, nitriles, isocyanates, isocyanides, nitrites, nitrosos, thiols, thioethers, sulfoxides, sulfonic acids, thiocyanates, isothiocyanates, thiones, thials, phosphines, phosphonic acids, phosphates, boronic acid, boronic esters, borinic acids, hetroaromatics, and heterocycles.

As is known in the art, a catalyst is a substance that increases the rate of a chemical reaction by reducing the activation energy, but which is left unchanged by the reaction. Various catalysts can be adapted for use with embodiments of the invention. For example, the catalyst in the polymerization reactions can be selected to control the equilibrium constant between the active and dormant species. This equilibrium determines the polymerization rate. Catalysts selected to have a small equilibrium constant can be used in contexts where it is desirable to inhibit or slow the polymerization reaction while catalysts selected to have a large equilibrium constant can be used in contexts where it is desirable to have a high distribution of chain lengths. In typical embodiments of the invention, the catalyst is a metal photoredox catalyst. For a review of photoredox catalysts see J. M. R. Narayanam, et al. Chem. Soc. Rev. 2011, 40, 102-113.

In one embodiment, the photoredox catalyst is selected from a group consisting of transition metal complexes. In certain embodiments, the amount of catalyst is less than 20 mol % but more than 0.00001 mol % relative to the amount of monomer used. In one particular embodiment, the photoredox catalyst is fac-Ir(ppy)$_3$.

Photoredox catalysts other than *fac*-Ir(ppy)₃ may also be used, which include but are not limited to those shown in Figure 14A-14C. Selected photoredox catalysts can include structures of the type $ML^1L^2L^3$, where L^1, L^2, and L^3 can be but are not limited to those shown in Figure 14D-14F. Transition metals other than Ir and Ru that

5   can be used as part of a selected photoredox catalyst complex include, but are not limited to, Cr, Co, Fe, Rh, Mn, Pt, Pd, Os, Eu, Cu, Al, Ti, Zn, Cd.

Photoredox catalysts are well known in the art (see, e.g. D. A. Nicewicz, et al. *Science* 2008, 322, 77–80). However, such catalysts have been used only for specific aspects of the polymerization process and not the whole process. Moreover, they

10   have only been successful as photoinitiators, employing light to initiate the reactions and not as a means to have precise control over the chain growth process of radical polymerizations, reversibly mediating initiation, polymerization and deactivation steps (see, e.g. Lalevee et al., ACS MACRO LETT., 286-290 (2012).

As disclosed herein, the unique properties of these photoredox catalysts can

15   now be used in systems and methods of highly responsive photocontrolled radical polymerization. By taking advantage of the unique properties that photoredox catalysts display, a free radical polymerization method and system is provided that can be efficiently controlled (e.g., reversibly activated/deactivated) by an external stimulus (light) with all of the desired attributes described above. Notably, this

20   invention can use sub-stoichiometric levels of a photoredox catalyst, has an uncomplicated and easy process setup, and is tolerant of reactive functional groups, such as carboxylic acids, epoxides, amines, etc, because of the robust nature of these catalysts. Because these functional groups have been shown to interfere with other radical procedures, this invention is highly attractive and has widespread application

25   in a number of fields.

In one illustrative aspect of the present invention, an exemplary photoredox mechanism for the controlled radical polymerization is shown in Figure 1. Photoredox catalysts (M, Figure 1) have been shown to absorb light to afford a complex in the excited state (M(n)*). This excited M(n)* species reduces the alkyl

halide or pseudo halide to give the desired alkyl radical, which undergoes polymerization with an alkene monomer that is chosen from typical alkene monomers that undergo traditional radical polymerization. The highly oxidizing M(n+l) complex then reacts with the alkyl radical to afford the initial M(n) complex in the ground state, as well as an alkyl halide/pseudo halide capped polymer. In certain embodiments, this process is repeated with the aid of an additional photon of light The oxidation of the radical to form the alkyl halide/pseudo halide chain end gives rise to a controlled and radical polymerization process.

Notably, this results in a photochemically controlled process. An advantage of this type of system, and one reason that sets it apart from traditional Cu-mediated ATRP methods, is the ability to reversibly activate or reversibly deactivate the polymerization with visible light. Specifically, when light is removed from this reaction no M(n)* will be present, therefore, the radical chain ends will be oxidized and the reaction will rest at the dormant and stable alkyl halide/pseudo halide species. Furthermore, upon re-exposure to light, M(n)* will be formed, re-activating the polymerization.

Various metals can be used in the design of the photoredox catalyst, with Ir and Ru being two examples. In one illustrative embodiment, the mechanism for photocontrolled radical polymerization is shown in Figure 4. *Fac*-[Ir(ppy)$_3$], a commercially available complex, has been shown to absorb visible light to afford *fac*-[Ir(ppy)$_3$]*. This excited Ir^{III}* species reduces an alkyl bromide initiator to give the desired alkyl radical, which initiates polymerization of the monomer. The highly oxidizing Ir^{IV} complex then reacts with the propagating radical to afford the initial Ir^{III} complex in the ground state, as well as a dormant polymer chain with a bromo end group. Having regenerated the starting Ir^{III} complex, homolysis of the C-Br bond, addition of monomer to the radical chain end and recapping with bromide thus occurs with the overall cyclic process being mediated by visible light. When light is removed from this reaction, no Ir^{III}* will be present, and the polymerization will rest at the dormant and stable bromo chain-terminated species. Furthermore, upon

reexposure to visible light, Ir^{III}* is formed, reactivating the polymerization and allowing for true control over polymer structure and architecture.

The following examples are given to aid in understanding the invention, but it is to be understood that the invention is not limited to the particular materials or procedures of examples. As discussed herein, it has been discovered that it is possible to modify and manipulate the disclosed polymerization processes in a manner that allows them to be used to form complex polymer structures. Moreover, it has been discovered that the rate of polymer formation in these processes is directly proportional to the amount of light to which the reaction is exposed, an unexpected characteristic that allows artisans to use light to easily and precisely control a variety of aspects of the processes as well as the polymeric compositions formed from these processes. Certain methods, materials and polymerization processes discussed herein are also disclosed in Fors et al., Angewandte Chemie Volume 51, Issue 35, pages 8850–8853 (2012).

EXAMPLES

The following Example(s) illustrate the versatility and scope of the embodiments of the instant invention.

EXAMPLE 1: ILLUSTRATIVE METHODS AND MATERIALS USEFUL IN LIGHT MEDIATED CONTROLLED RADICAL POLYMERIZATION REACTIONS

Radical polymerizations have become a powerful and widely utilized synthetic tool for the formation of well-defined polymers that are diverse in their structure and function. The capability to regulate these processes by an external stimulus would greatly increase their applicability across a number of fields and allow for the synthesis of previously inaccessible macromolecular structures. On this basis, a radical polymerization that can be efficiently and reversibly activated or deactivated by light has been developed. This new polymerization process is highly responsive to

the external stimulus (light) and allows for both temporal and spatial control over the chain growth process.

As disclosed in Fors et al., Angewandte Chemie Volume 51, Issue 35, pages 8850–8853 (2012), the polymerization of methyl methacrylate (MMA) was examined by using the Ir complex 1 (*fac*-[Ir(ppy)₃]) as the catalyst, ethyl-α-bromophenylacetate as the initiator, and a 50 W fluorescent lamp as the light source. In keeping with the simple, user friendly nature of aspects of the invention, complex 1 was selected for preliminary studies owing to its stability, highly reducing nature, and commercial availability. Encouragingly, initial results employing 0.2 mol% catalyst did afford polymer; however, the reaction displayed little to no control, with a M_w/M_n value of 2.76 (Figure 5, entry 1). It was reasoned that photoredox catalyst 1 was only acting as an initiator in this reaction, and to gain control over this system the radical concentrations needed to be lowered, which could be achieved by simply reducing the catalyst loading. In support of this hypothesis, it was found that significantly decreasing the loading from 1 to 0.005 mol% led to excellent control over the polymerization with a molecular weight distribution of 1.25 being obtained (Figure 5, entry 2); this low catalyst loading is a highly desirable feature. Further, under the optimized reaction conditions, subsequent polymerizations demonstrated that the molecular weight of the polymer could be efficiently controlled by changing the monomer/initiator ratio with close agreement between the experimental and theoretical molecular weights (Figure 5, entries 2–5).

To confirm the proposed mechanism, control polymerizations were conducted without added catalyst or in the absence of light, and in both examples no reaction was observed (Figure 5, entries 6 and 7). Additional supporting evidence was obtained through fluorescence studies. When 1 was combined with various concentrations of MMA, no change in the fluorescence of the Ir complex was detected. However, when the same experiment was performed with the initiator, ethyl-α-bromophenylacetate, a concentration-dependent fluorescence quenching was observed. These results suggest

that the excited $Ir^{III}*$ complex is undergoing a redox process with the initiator and not reacting with the monomer.

The lack of any reaction in the absence of visible light suggests that a true "on"–"off" photopolymerization system could be developed. To demonstrate this possibility, monomer, initiator, and catalyst were initially combined in the absence of light and after one hour no polymerization was observed. The reaction was then exposed to visible light for two hours at room temperature, which resulted in approximately 15% monomer conversion. In demonstrating true temporal control, removal of the light source stops the polymerization immediately and no conversion was observed during the dark period (1 hour). Exposure to light for a second two-hour period "turns" the polymerization back on and this "on"/"off" cycle can be repeated numerous times without observable reaction in the absence of irradiation (Figure 2a). These results demonstrate that this system is highly responsive to the external stimulus and when light is removed from the system polymerization stops almost immediately. This high degree of temporal control illustrates the efficient nature of the *fac*-[Ir(ppy)$_3$] catalyst for reversible activation and deactivation of the bromo chain end.

To clearly demonstrate that existing chain ends are reactivated during these "on"/"off" cycles with no new chains being initiated during the polymerization, plots of $\ln([M]_0/[M]_t)$ versus total exposure time (Figure 2b), and M_n versus conversion (Figure 2c) both gave linear relationships. Significantly, this data proves that when the light is turned off and polymerization stops, termination of the chain ends is not occurring and in the absence of light, the dormant species is the stable bromo chain end. In comparison with ATRP, when these dormant chain ends are reexposed to light in the presence of the iridium catalyst, efficient reactivation of the chain ends is achieved. These features demonstrate that this process is a photocontrolled radical polymerization, which is highly responsive to visible light as an external stimulus (the reaction has been kept in the dark for up to five hours without any observed loss of the active reversible nature of the polymerization process).

To further probe the nature of this system, as well as demonstrate the presence of active bromo groups at the chain ends, block copolymers were prepared using sequential photocontrolled radical procedures (Figure 3). Initially, irradiation of a mixture of methyl methacrylate and the initiator 2 (ethyl α-bromophenylacetate) in the presence of the iridium photocatalyst 1 (0.005 mol%) afforded a well-defined PMMA derivative, 3, with controlled molecular weight and low polydispersity. Use of 3 as a macroinitiator in the polymerization of benzyl methacrylate and in this case, 0.01 mol% of 1, proved to be a well-behaved process leading to the desired poly(methyl methacrylate)-b-(benzyl methacrylate) diblock copolymer 4, with size exclusion chromatography showing little or no starting macroinitiator (Figure 3). This efficient block copolymer formation further illustrates that minimal termination is occurring during the polymerization process.

A major difference between the reported photocontrolled radical polymerization and ATRP procedures is the stability of the catalyst, with the Ir-based system being extremely tolerant to a variety of functional groups. To demonstrate this added versatility, the synthesis of homopolymers of methacrylic acid (MAA), which is notoriously difficult to polymerize under ATRP conditions, and random copolymers of MAA and benzyl methacrylate (BnMA) were examined. Under standard conditions and at 10% incorporation of MAA, excellent control over molecular weight and a low polydispersity were observed. Moreover, the polydispersity increased only slightly with higher MAA content (Figure 6). These polymerizations in the presence of a free carboxylic acid exemplify the robust nature of the Ir-based catalyst 1. Moreover, this excellent functional-group tolerance is an additional advantage over ATRP processes.

Additionally, when 1 was combined with various concentrations of MMA, no change in the fluorescence of the Ir-complex was detected. However, when the same experiment was performed with the initiator, ethyl α-bromophenylacetate, a concentration dependent fluorescence quenching was observed. These results

demonstrate that the excited Ir(III)* complex is undergoing a redox process with the initiator and not reacting with the monomer.

Illustrative Reagent Information

5   All reactions were carried out under an argon atmosphere. The dimethyl formamide (DMF) was purchased from Fischer Scientific and vigorously purged with argon. The solvent was further purified by passing it under argon pressure through a Pure Solv 400-3-MD solvent purification system. Methyl methacrylate (MMA), benzyl methacrylate (BnMA) and methacrylic acid (MAA) were purchased from

10   Sigma-Aldrich and passed through a plug of basic alumina and filter agent before use. Complex 1 [*fac*-Ir(ppy)₃] and ethyl α-bromophenylacetate were purchased from Sigma-Aldrich and used as received. 50-Watt fluorescent lamps were used as the light source.

15   *Illustrative Analytical Information*

Nuclear magnetic resonance spectra were recorded on a Varian 400 MHz, a Varian 500 MHz or a Varian 600 MHz instrument. All ^{1}H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated.

20   All ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), unless otherwise stated, and all were obtained with ^{1}H decoupling. Gel permeation chromatography (GPC) was performed on a Waters 2695 separation module with a Waters 2414 refractive index detector in chloroform with 0.25% triethylamine. Number average molecular weights (M_n) and weight average molecular weights (M_w)

25   were calculated relative to linear polystyrene standards.

Illustrative Light Source

All reactions were placed within 3 cm of two 50 W fluorescent lamps, which were on either side of the reaction. In order to obtain a value for the intensity of light

that is absorbed by the catalyst in these reactions a monochromatic light source (blue LED's; λ = 435 nm) was used. At a distance of 1 inch from the LED's the polymerizations showed a similar kinetic profile to the same reaction using the fluorescent lamps. The intensity of the light 1-inch from the blue LED's was found to be 0.5 mW/cm^2. For these studies the blue LED's were purchased from Creative Lighting Solutions.

General Procedure Followed to Obtain Data Presented in Figure 5
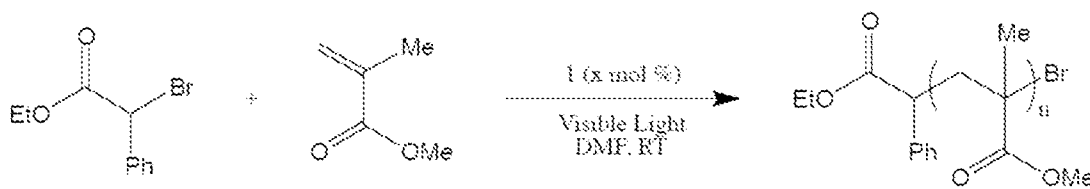
The scheme above provides drawings of aspects of this reaction. A vial, which was equipped with a magnetic stir bar and fitted with a teflon screw cap septum, was charged with MMA (401 µL, 3.75 mmol), complex 1 (0 – 0.2 mol %) and DMF (1.4 mL). The reaction mixture was degassed by freeze-pump-thaw cycles (this process was repeated a total of 3 times). The vial was then backfilled with argon and ethyl α-bromophenylacetate (0.002 – 0.2 equiv) was injected via syringe. The reaction was stirred in front of a 50 W fluorescent lamp (see Figure 7) until it reached ca. 50% conversion of the MMA as monitored by ^{1}H NMR. An aliquot was then removed from the reaction mixture and analyzed by GPC to give the number average molecular weight (M$_n$), weight average molecular weight (M$_w$) and molecular weight distribution (M$_w$/M$_n$) of the polymer.

Illustrative Fluorescence Quenching Studies

A Varian Cary Eclipse Fluorescence Spectrophotometer was used for the quenching studies. The Ir(ppy)$_3$ (complex 1) solutions were excited at 334 nm. The emission of a 0.13 mM solution of complex 1 in DMF was first measured at varying concentrations of MMA (0 – 112 mM). As shown in Figures 8 and 9 no quenching of

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the emission of complex 1 was observed at any of the concentrations of MMA. The emission of a 0.13 mM solution of complex 1 in DMF was also measured at varying concentrations of ethyl α- bromophenylacetate (0 – 136 mM). As shown in Figures 9 and 10 a concentration dependent fluorescence quenching was observed.

Reaction Monitoring for Optimized Conditions Presented in **Figure 5**
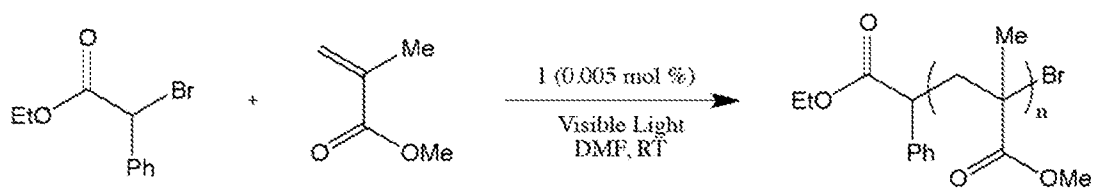
The scheme above provides drawings of aspects of this reaction. A vial, which was equipped with a magnetic stir bar and fitted with a teflon screw cap septum, was charged with MMA (401 μL, 3.75 mmol), complex 1 (0.123 mg, 0.005 mol %) and DMF (1.4 mL). The reaction mixture was degassed by freeze-pump-thaw cycles (this process was repeated a total of 3 times). The vial was then backfilled with argon and ethyl α-bromophenylacetate (2.62 μL, 0.015 mmol) was injected via syringe. The reaction was stirred in front of a 50 W fluorescent lamp, and aliquots were removed from the reaction mixture via syringe under a positive pressure of argon at different time points. The samples were analyzed by ^{1}H NMR to give the conversion of MMA and GPC to give the number average molecular weight (M_n), weight average molecular weight (M_w) and molecular weight distribution (M_w/M_n) of the polymer. For data see Figure 11 and Figure 12.

General Procedure Followed to Obtain Data Presented in Figure 2

A vial, which was equipped with a magnetic stir bar and fitted with a septum, was charged with MMA (1.20 mL, 11.25 mmol), complex 1 (0.37 mg, 0.005 mol %) and DMF (4.2 mL). The reaction mixture was degassed by freeze-pump-thaw cycles (this process was repeated a total of 3 times). The vial was then backfilled with argon, covered in aluminum foil and ethyl α-bromophenylacetate (2.62 μL, 0.015 mmol) was injected via syringe. The reaction was stirred in the absence of light. After 1 hour an

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aliquot was removed from the reaction mixture via syringe under a positive pressure of argon. The vial was then placed in front of a 50 W fluorescent lamp and allowed to stir. After 2 hours an additional aliquot was removed from the reaction mixture and the vial was immediately covered with aluminum foil and stirred in the absence of

5   light. This process was then repeated several times (see Figure 2). The samples were analyzed by ^{1}H NMR to give the conversion of MMA and GPC to give the number average molecular weight (M_n), weight average molecular weight (M_w) and molecular weight distribution (M_w/M_n) of the polymer.

10   *General Procedure Followed to Obtain Data Presented in Figure 3*
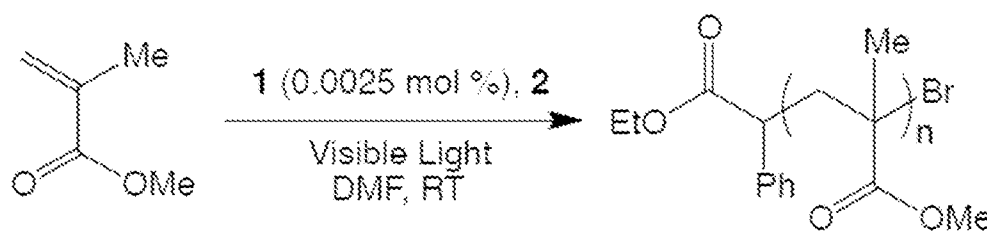
The scheme above provides drawings of aspects of this reaction for producing poly(methyl methacrylate). A vial, which was equipped with a magnetic stir bar and fitted with a septum, was charged with MMA (2.4 mL, 22.5 mmol), complex 1 (1.4

15   mg, 0.005 mol %) and DMF (8.4 mL). The reaction mixture was degassed by freeze-pump-thaw cycles (this process was repeated a total of 3 times). The vial was then backfilled with argon and ethyl α-bromophenylacetate (15.7 μL, 0.09 mmol) was injected via syringe. The reaction was stirred in front of a 50 W fluorescent lamp for 4 hours and then covered with aluminum foil for 5 minutes. While still covered with the

20   aluminum foil the reaction mixture was transferred via cannula to an erlenmeyer flask containing a cold mixture of methanol and water (10:1, 300 mL) that was being vigorously stirred. A white precipitate formed, which was filtered, taken up in a minimal amount of CH_2Cl_2 and precipitated a second time from a cold mixture of methanol and water (10:1, 300 mL). The white precipitate was then filtered and dried

25   to give 423 mg of the desired product. This product was used as the macroinitiator in

the reaction that is described in the next section. M_n = 7800 g/mol, M_w/M_n = 1.28; ^{1}H

NMR (500 MHz, CDCl$_3$) δ: 3.57 (s, 3H), 1.96 – 1.72 (m, 1.7H), 1.40 (m, 0.16H), 1.16

(m, 0.12H), 1.00 (s, 1H), 0.82 (bs, 2H) ppm. 13C NMR (500 MHz, CDCl$_3$) δ: 178.1,

177.8, 177.0, 54.4, 54.2, 51.8, 44.9, 44.5, 18.7, 16.4 ppm. IR (neat, cm^{-1}): 2990, 2950,
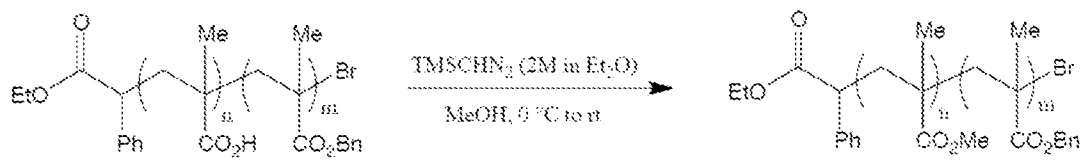
1727, 1435, 1270, 1240, 1191, 988, 841, 749.
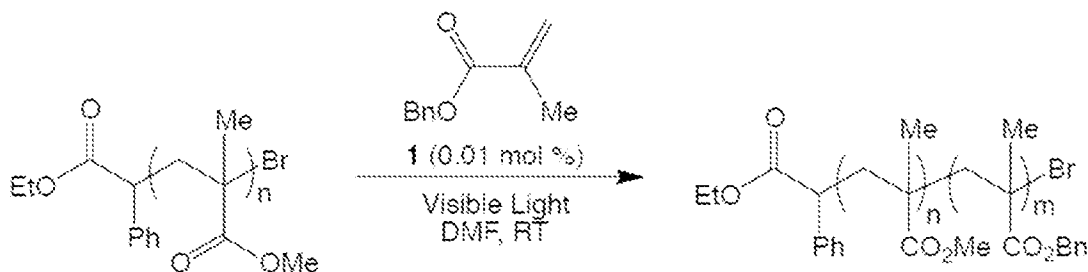
The scheme above provides drawings of aspects of this reaction for producing

poly(methyl methacrylate)-*b*-(benzyl methacrylate). A vial, which was equipped with

a magnetic stir bar and fitted with a septum, was charged with benzyl methacrylate

(635 μL, 3.75 mmol), the macroinitiator (111 mg, 0.015 mmol) and DMF (1.4 mL).

The reaction mixture was degassed by freeze-pump-thaw cycles (this process was

repeated a total of 3 times). The vial was then backfilled with argon and a solution of

complex 1 in DMF (200 μL, 0.01 mol %), which had been degassed in an analogous

fashion as described for the reaction mixture above, was injected via syringe. The

reaction was stirred in front of a 50 W fluorescent lamp for 5 hours and then covered

with aluminum foil for 5 minutes. The reaction mixture was then added in a dropwise

fashion to an erlenmeyer flask containing a mixture of cold methanol and water (10:1,

200 mL) that was being vigorously stirred. A white precipitate formed, which was

filtered, taken up in a minimal amount of CH$_2$Cl$_2$ and precipitated a second time from

a cold mixture of methanol and water (10:1, 200 mL). The white precipitate was then

filtered and dried to give 392 mg of the desired product. M_n = 30,600 g/mol, M_w/M_n =

1.30; ^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.26 (s, 10.5H), 4.89 (bs, 4.26H), 3.61 (s, 3H),

2.00 -1.63 (m, 5.26H) 1.03 (s, 0.76H), 0.89 (m, 3.7H), 0.71 (s, 4.28H) ppm. 13C

NMR (500 MHz, CDCl$_3$) δ: 177.0, 135.4, 135.2, 128.5, 128.4, 128.2, 66.7, 54.4, 51.7,

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45.1, 44.8, 44.6, 18.8, 16.6 ppm. IR (neat, cm^{-1}): 2949, 1725, 1454, 1387, 1239, 1141, 966, 912, 749, 696.

General Procedure Followed to Obtain Data Presented in Figure 6
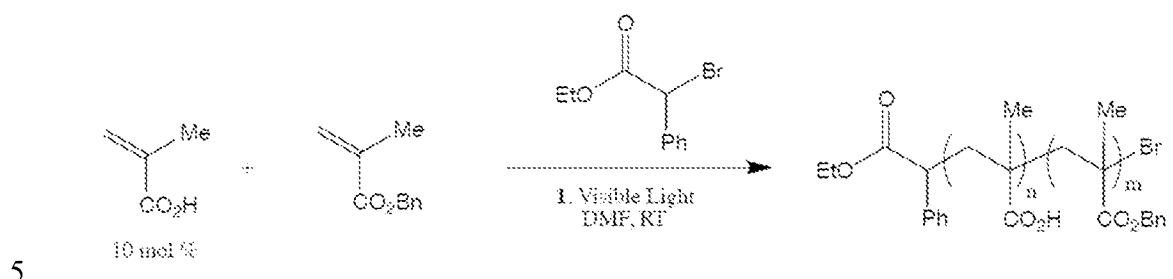
The scheme above provides drawings of aspects of this reaction for producing poly(benzyl methacrylate-ran-methacrylic acid) (Figure 6, entry 1). A vial, which was equipped with a magnetic stir bar and fitted with a septum, was charged with benzyl methacrylate (1.14 mL, 6.75 mmol), methacrylic acid (63 µL, 0.75 mmol, 10 mol %), complex 1 (0.25 mg, 0.005 mol%) and DMF (2.8 mL). The reaction mixture was degassed by freeze-pump-thaw cycles (this process was repeated a total of 3 times). The vial was then backfilled with argon and ethyl α-bromophenylacetate (5.24 µL, 0.030 mmol) was injected via syringe. The reaction was stirred in front of a 50 W fluorescent lamp for 5 hours (^{1}H NMR of the crude reaction mixture showed ca. 50% conversion of the benzyl methacrylate). The reaction mixture was then added dropwise to cold diethyl ether (250 mL) that was being vigorously stirred. An off-white precipitate formed, which was filtered, taken up in a minimal amount of CH$_2$Cl$_2$ and was precipitated a second time from cold diethyl ether (250 mL). The off-white precipitate was then filtered and dried to give 475 mg of the desired product. ^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.27 (s, 5H), 4.87 (bs, 2H), 2.05 – 1.65 (m, 1.87H), 1.43 – 1.05 (m, 0.37H), 0.91 (s, 1.34H), 0.73 (s, 1.8H) ppm. ^{13}C NMR (500 MHz, CDCl$_3$) δ: 177.1, 176.4, 135.4, 135.1, 129.0, 128.5, 128.4, 128.2, 125.3, 66.8, 54.1, 45.1, 44.8, 18.5, 16.6 ppm. IR (neat, cm^{-1}): 2949, 1722, 1454, 1387, 1236, 1138, 963, 911, 747.

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The scheme above provides drawings of aspects of this reaction. In order to further characterize the random copolymer of benzyl methacrylate and methacrylic acid by GPC it was methylated to afford poly(benzyl methacrylate-ran-methyl methacrylate) (see, e.g. E. Kühnel et al. *Angew. Chem. Int. Ed.* 2007, 46, 7075–7078). A vial, which was equipped with a magnetic stir bar and fitted with a septum, was charged with the poly(benzyl methacrylate-ran-methacrylic acid) (20 mg). The reaction vessel was purged with argon and then methanol was added via syringe (1.5 mL). The reaction mixture was cooled to 0 °C and then solution of TMSCHN$_2$ (300 μL, 2M in diethyl ether) was added dropwise over a 5 minute period. The reaction was warmed to room temperature and allowed to stir for 4 hours. Acetic acid (100 μL) was then added slowly to the reaction mixture to quench the excess TMSCHN$_2$ (^{1}H NMR of the crude reaction mixture showed ca. 9 mol % incorporation of the methacrylic acid). The solvent and byproducts of the reaction were then removed under vacuum for a 16-hour period to give the desired product, which was analyzed by GPC. M_n = 21,000 g/mol, M_w/M_n = 1.24.
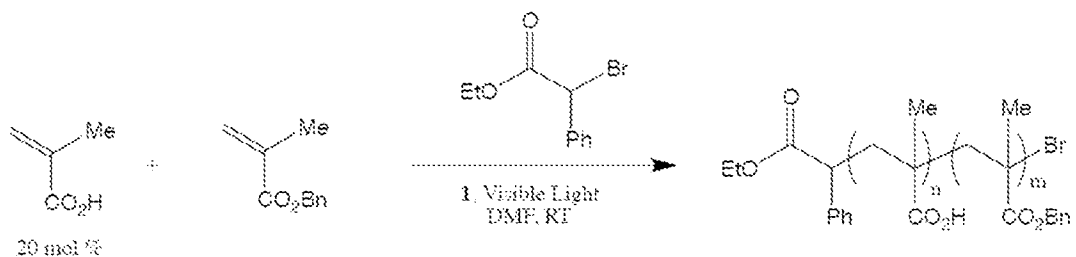
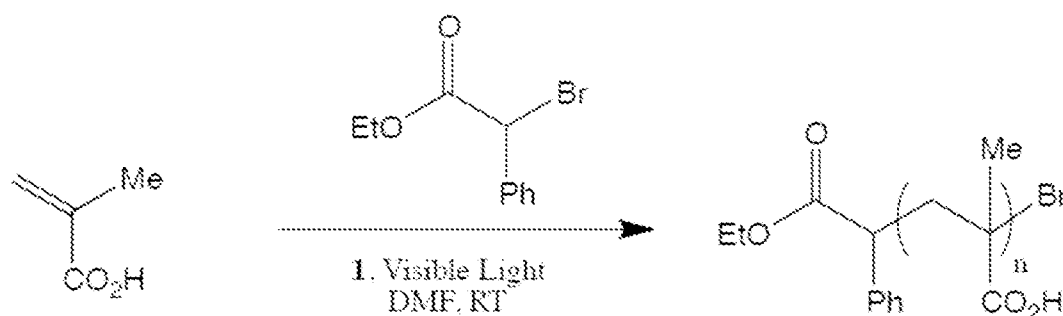The scheme above provides drawings of aspects of this reaction for producing poly(benzyl methacrylate-ran-methacrylic acid) (Figure 6, entry 2). A vial, which was equipped with a magnetic stir bar and fitted with a septum, was charged with benzyl methacrylate (1.14 mL, 6.75 mmol), methacrylic acid (128 μL, 0.75 mmol, 20 mol %), complex 1 (0.25 mg, 0.005 mol%) and DMF (2.8 mL). The reaction mixture

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was degassed by freeze-pump-thaw cycles (this process was repeated a total of 3 times). The vial was then backfilled with argon and ethyl α-bromophenylacetate (5.24 μL, 0.030 mmol) was injected via syringe. The reaction was stirred in front of a 50 W fluorescent lamp for 5 hours (^{1}H NMR of the crude reaction mixtures showed ca. 50%

5   conversion of the benzyl methacrylate). The reaction mixture was then added dropwise to cold diethyl ether (250 mL) that was being vigorously stirred. An off-white precipitate formed, which was filtered, taken up in a minimal amount of CH_2Cl_2 and was precipitated a second time from cold diethyl ether (250 mL). The off-white precipitate was then filtered and dried to give 457 mg of the desired product. ^{1}H NMR

10   (500 MHz, $CDCl_3$) δ: 7.27 (s, 5H), 4.80 (bs, 2H), 2.05 – 1.40 (m, 1.64H), 1.38 – 1.05 (m, 0.35H), 0.95 – 0.20 (m, 3.47H) ppm. 13C NMR (500 MHz, $CDCl_3$) δ: 177.0, 135.4, 135.1, 128.5, 128.2, 66.8, 54.0, 45.1, 44.8, 16.3 ppm. IR (neat, cm^{-1}): 3030, 2946, 1722, 1454, 1386, 1237, 1138, 964, 746, 692.
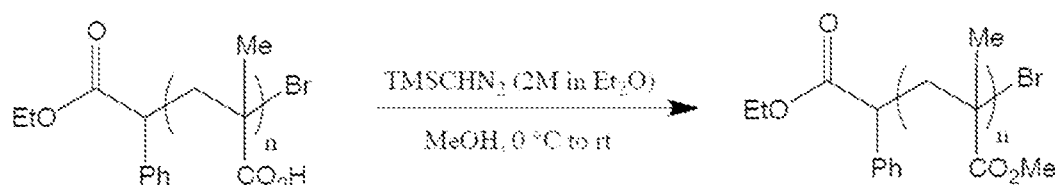

15   The scheme above provides drawings of aspects of this reaction. In order to further characterize the random copolymer of benzyl methacrylate and methacrylic acid by GPC it was methylated to afford poly(benzyl methacrylate-ran-methyl methacrylate) (see, e.g. E. Kühnel et al. *Angew. Chem. Int. Ed.* 2007, 46, 7075–7078). A vial, which was equipped with a magnetic stir bar and fitted with a septum, was

20   charged with the poly(benzyl methacrylate-ran-methacrylic acid) (20 mg). The reaction vessel was purged with argon and then methanol was added via syringe (1.5 mL). The reaction mixture was cooled to 0°C and then solution of TMSCHN$_2$ (300 μL, 2M in diethyl ether) was added dropwise over a 5 minute period. The reaction was warmed to room temperature and allowed to stir for 4 hours. Acetic acid (100 μL)

25   was then added slowly to the reaction mixture to quench the excess TMSCHN$_2$ (^{1}H NMR of the crude reaction mixture showed ca. 16 mol % incorporation of the methacrylic acid). The solvent and byproducts of the reaction were then removed

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under vacuum for a 16-hour period to give the desired product, which was analyzed by GPC. M_n = 22,000 g/mol, M_w/M_n = 1.36.

The scheme above provides drawings of aspects of this reaction for producing poly(methacrylic acid) (Figure 6, entry 3) A vial, which was equipped with a magnetic stir bar and fitted with a septum, was charged with methacrylic acid (317 μL, 3.75 mmol), complex 1 (3.1 mg) and DMF (1.0 mL). The reaction mixture was degassed by freeze-pump-thaw cycles (this process was repeated a total of 3 times). The vial was then backfilled with argon and ethyl α-bromophenylacetate (2.62 μL, 0.015 mmol) was injected via syringe. The reaction was stirred in front of a 50 W fluorescent lamp for 72 hours. The reaction mixture was then added dropwise to cold diethyl ether (100 mL) that was being vigorously stirred. An off-white precipitate formed, which was filtered, taken up in a minimal amount of CH_2Cl_2 and was precipitated a second time from cold diethyl ether (100 mL). The white precipitate was then filtered and dried to give 110 mg of the desired product. ^{1}H NMR (600 MHz, CD_3OD) δ: 2.14 – 1.78 (m, 1.86H), 1.54 (bs, 0.13H), 1.22 – 1.05 (m, 3H) ppm. ^{13}C NMR (600 MHz, CD_3OD) δ: 180.8, 179.9, 54.1, 48.4, 44.9, 44.5, 17.8, 15.9 ppm. IR (neat, cm^{-1}): 3165, 2990, 1698, 1481, 1448, 1389, 1259, 1168, 961, 929, 796.

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The scheme above provides drawings of aspects of this reaction. In order to further characterize the polymethacrylic acid by GPC it was methylated to afford poly(methyl methacrylate). A vial, which was equipped with a magnetic stir bar and fitted with a septum, was charged with the poly(methacrylic acid) (10 mg). The

5   reaction vessel was purged with argon and then methanol was added via syringe (2 mL). The reaction mixture was cooled to 0 °C and then solution of TMSCHN$_2$ (400 μL, 2M in diethyl ether) was added dropwise over a 5 minute period. The reaction was warmed to room temperature and allowed to stir for 4 hours. Acetic acid (100 μL) was then added slowly to the reaction mixture to quench the excess TMSCHN$_2$. The

10   solvent and byproducts of the reaction were then removed under vacuum for a 16-hour period to give the desired product, which was analyzed by GPC. M_n = 28,500 g/mol, M_w/M_n = 1.61.

       All numbers recited in the specification and associated claims that refer to

15   values that can be numerically characterized with a value other than a whole number (e.g. a distance) are understood to be modified by the term "about". Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limit of that range and any other stated or intervening value in that stated range,

20   is encompassed within the invention. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges, and are also encompassed within the invention, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the invention.

25   Furthermore, all publications mentioned herein are incorporated herein by reference to disclose and describe the methods and/or materials in connection with which the publications are cited. Publications cited herein are cited for their disclosure prior to the filing date of the present application. Nothing here is to be construed as an admission that the inventors are not entitled to antedate the publications by virtue of

an earlier priority date or prior date of invention. Further the actual publication dates may be different from those shown and require independent verification.

CLAIMS

1.   A composition of matter comprising:
        a plurality of polymer chains, wherein the polymer chains undergo a radical
5   polymerization process that is reversibly activated in the presence of light and
reversibly deactivated in the absence of light.

2.   The composition of claim 1, wherein the polymer chains exhibit a
polydispersity resulting from exposure to a first amount of light wherein M_w/M_n is
10   between 1.0 and 2.0, wherein M_w = the weight average molecular weight of the
plurality of polymer chains; and M_n = the number average molecular weight of the
plurality of polymer chains.

3.   The composition of claim 1, wherein the composition comprises:
15   monomers that form the polymer chains in the radical polymerization process;
             an initiator that reacts with the monomers in the radical polymerization
process to form an intermediate compound capable of linking successively with the
monomers to form the polymer chains; and
             a photoredox catalyst.
20
4.   The composition of claim 3, wherein:
        the monomers comprise an alkene moiety;
        the initiator comprises an alkyl halide or pseudo halide moiety; and/or
        the photoredox catalyst comprises a transition metal selected from the group
25   consisting of Ir and Ru.

5.   The composition of claim 3, wherein the initiator is present in the composition
in a sub-stoichiometric amount.

6.   The composition of claim 3, wherein the photoredox catalyst is present in the composition in a sub-stoichiometric amount.

7.   The composition of claim 3, wherein the amount of catalyst is less than 20 mol % but more than 0.00001 mol % relative to the amount of monomer used.

8.   The composition of claim 1, wherein the plurality of polymer chains comprise at least one of: random copolymers, block copolymers or graft copolymers.

9.   The composition of claim 1, wherein the plurality of polymer chains consist essentially of block copolymers.

10.   A method of forming polymer chains comprising the steps of:
        (a) combining:
                monomers that form polymer chain subunits in a radical polymerization process;
                an initiator that reacts with monomers in the radical polymerization process to form an intermediate compound capable of linking successively with the monomers to form the polymer chains; and
                a photoredox catalyst; and
        (b) exposing compounds combined in (a) to light such that the radical polymerization process is initiated,
        so that the polymer chains are formed, wherein:
                the polymer chains undergo a radical polymerization process that is reversibly activated in the presence of light and reversibly deactivated in the absence of light.

11.   The method of claim 10, wherein polymer chain lengths are controlled by:

controlling an amount of time that compounds combined in (a) are exposed to light; and/or

controlling an intensity of light that reaches compounds combined in (a).

5   12.   The method of claim 10, wherein molecular weight distributions of the polymer chains are controlled by:

controlling an amount of time that compounds combined in (a) are exposed to light; and/or

controlling an intensity of light that reaches compounds combined in (a).

10

13.   The method of claim 12, wherein the method comprises exposing the polymer chains in to light so that the polymer chains exposed to light exhibit a polydispersity such that M_w/M_n is between 1.0 and 2.0, wherein M_w = the weight average molecular weight of the plurality of polymer chains; and M_n = the number average molecular

15   weight of the plurality of polymer chains.

14.   The method of claim 10, wherein polymer chain architecture is controlled by:

controlling an amount of time that compounds combined in (a) are exposed to light; and/or

20   controlling an intensity of light that reaches compounds combined in (a).

15.   The method of claim 10, wherein a sub-stoichiometric amount of initiator or photoredox catalyst is used in the compounds combined in (a).

25   16.   The method of claim 10, wherein the method comprises the sequential steps of:

exposing compounds combined in (a) to light for a period of time so that the radical polymerization process is activated;

protecting compounds combined in (a) from light exposure for a period of time so that the radical polymerization process is deactivated; and

re-exposing the compounds combined in (a) to light for a period of time so that the radical polymerization process is re-activated.

5

17.   A polymerization system comprising:

monomers that form polymer chain subunits in a radical polymerization process;

an initiator that reacts with monomers in the radical polymerization

10   process to form an intermediate compound capable of linking successively with the monomers to form the polymer chains; and

a catalyst;

wherein the monomers, initiator and catalyst can be combined in a reaction mixture that forms a plurality of polymer chains that undergo a radical polymerization

15   process that is reversibly activated in the presence of light and reversibly deactivated in the absence of light.

18.   The polymerization system of claim 17, further comprising:

a solvent in which the monomers, initiator and catalyst can be combined in the

20   reaction mixture;

a reaction vessel in which the monomers, initiator and catalyst can be combined so as to form the plurality of polymer chains;

a light source, wherein the amount and/or intensity of light produced by the light source is controllable; or

25   a filter that modulates the intensity of the light from the light source.

19.   The polymerization system of claim 17, wherein:

the monomer comprises a methacrylate, an acrylate, a styrene, a vinyl acetate, a vinylpyridine or a vinyl chloride;

the initiator comprises a halide or a pseudo halide; and

the catalyst comprises a transition metal photoredox catalyst having a transition metal selected from the group consisting of Ir and Ru.

5   20.   The polymerization system of claim 17, wherein monomers, initiator and catalyst are disposed together within a kit comprising a plurality of containers.
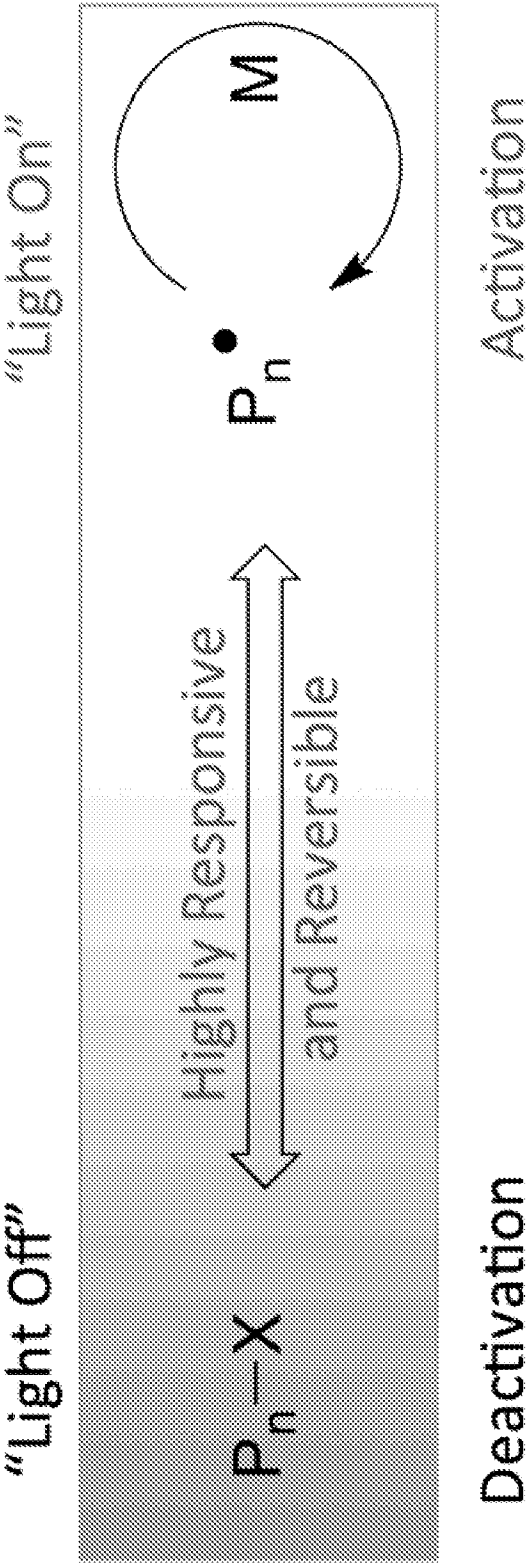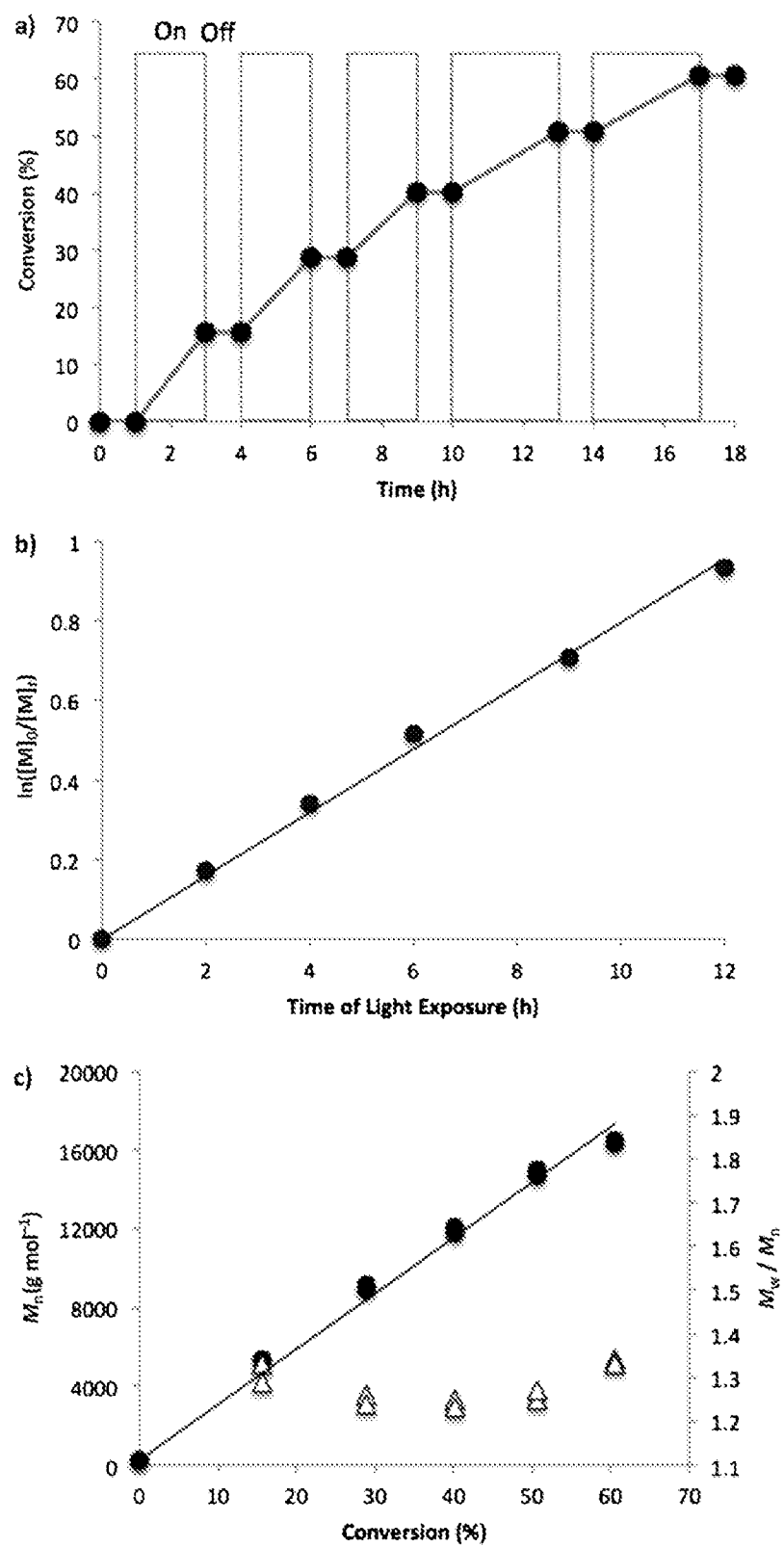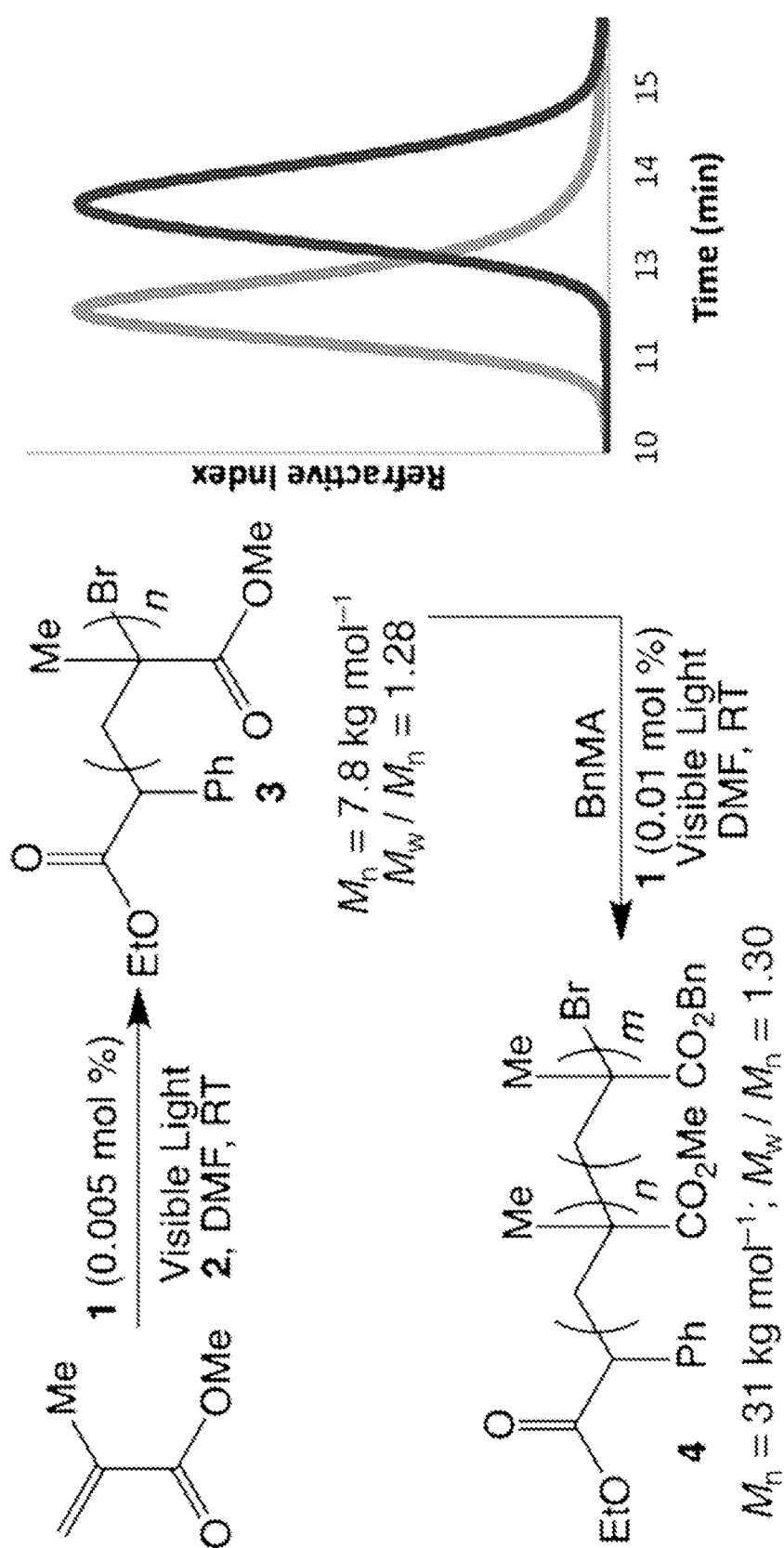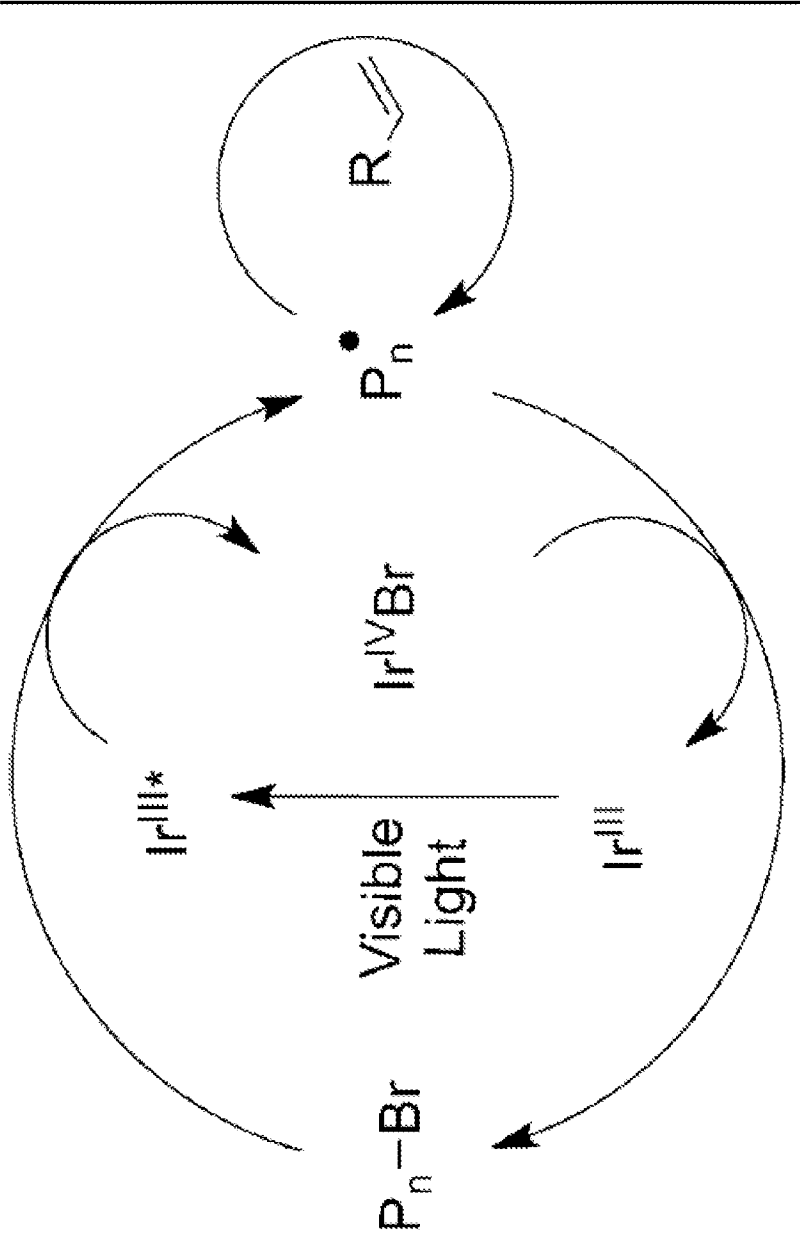
FIG. 1

FIG. 2

FIG. 3

FIG. 4

| Entry	1 [mol%]	M_n (experimental) [kg mol^{-1}]	M_n (theoretical) [kg mol^{-1}]	M_w/M_n
1	0.2	40.3	25.0	2.76
2	0.005	22.9	20.0	1.25
3	0.005	12.0	11.0	1.23
4	0.005	6.3	5.6	1.19
5	0.005	2.9	2.5	1.22
6	0	0	—	—
7[b]	0.005	0	—	—

[a] Reaction conditions: MMA (1 equiv), **1** (0–0.2 mol%), and **2** (0.002–0.20 equiv) in DMF (0.37 mL mmol^{-1} of MMA) at room temperature with irradiation from a 50 W fluorescent lamp (M_n = number average molecular weight; M_w = weight average molecular weight). [b] The reaction was run in the absence of visible light.

FIG. 5

Entry	MAA:BnMA	M_n [kg mol^{-1}]	M_w/M_n
1	10:90	21	1.24
2	20:80	22	1.36
3	100:0	28	1.61

[a] Reaction conditions: MAA (0.1–1.0 equiv), BnMA (0–0.90 equiv), **1** (0.005–0.13 mol%), and **2** (0.004 equiv) in DMF (0.37 mL mmol^{-1} of monomer) at room temperature with irradiation from a 50 W fluorescent lamp; for characterization the polymers were methylated after polymerization with TMSCHN$_2$ (TMS=trimethylsilyl) to give the methyl ester.

FIG. 6
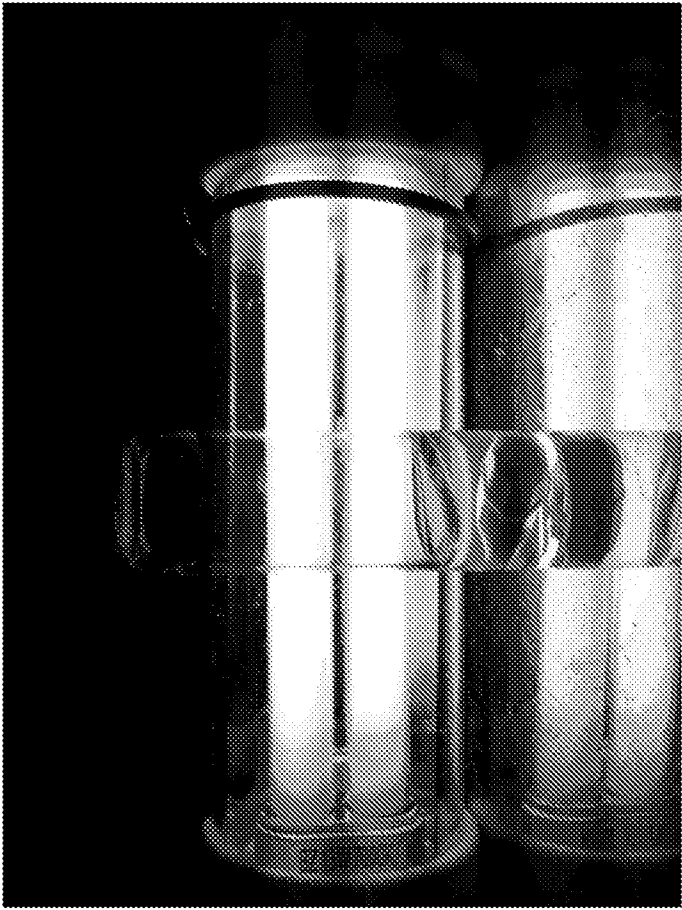
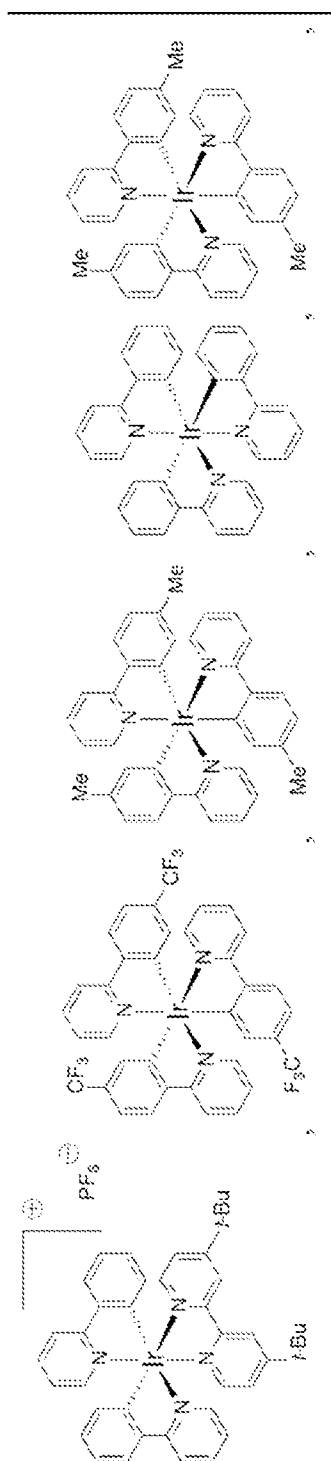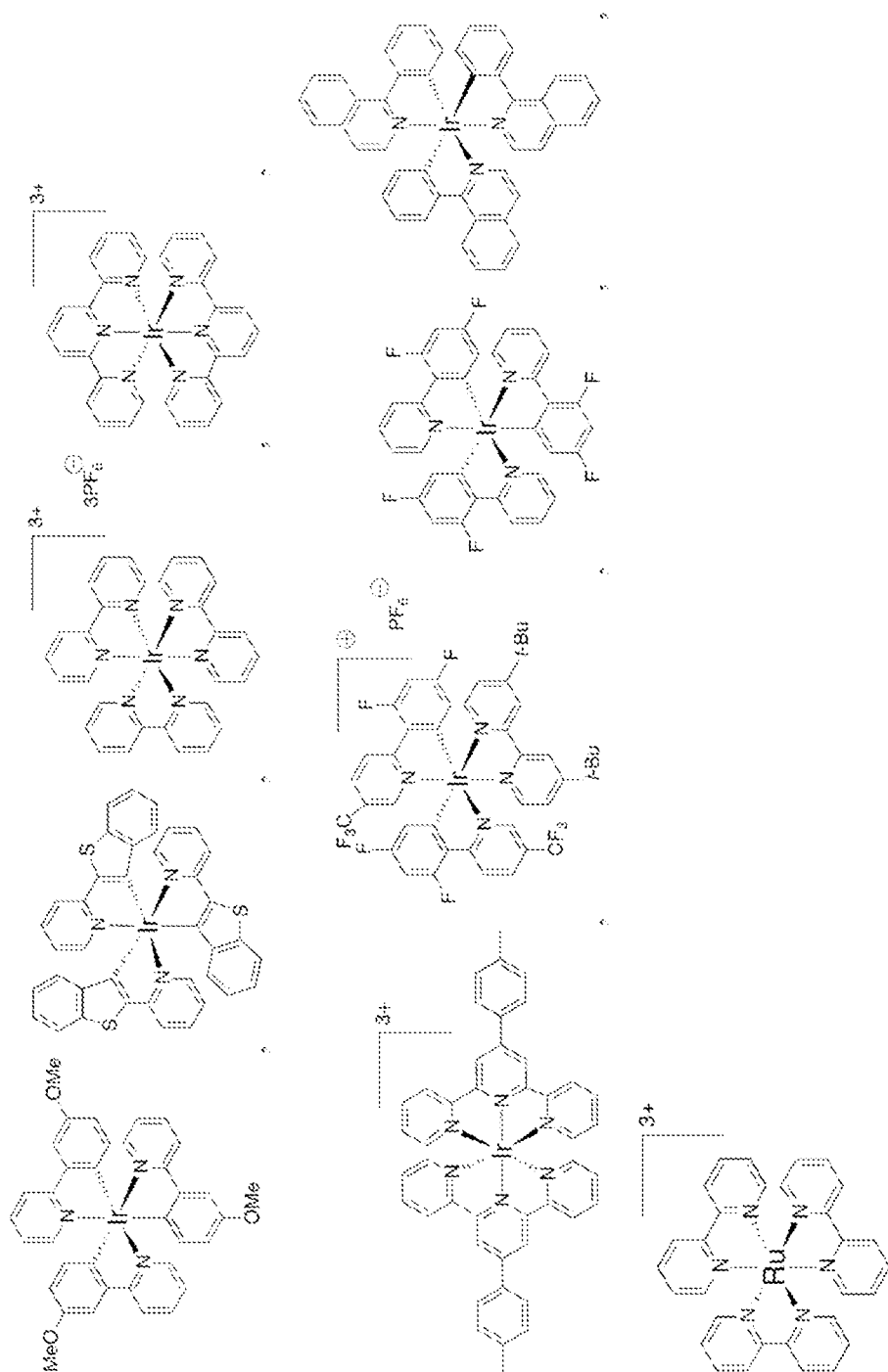FIG. 7
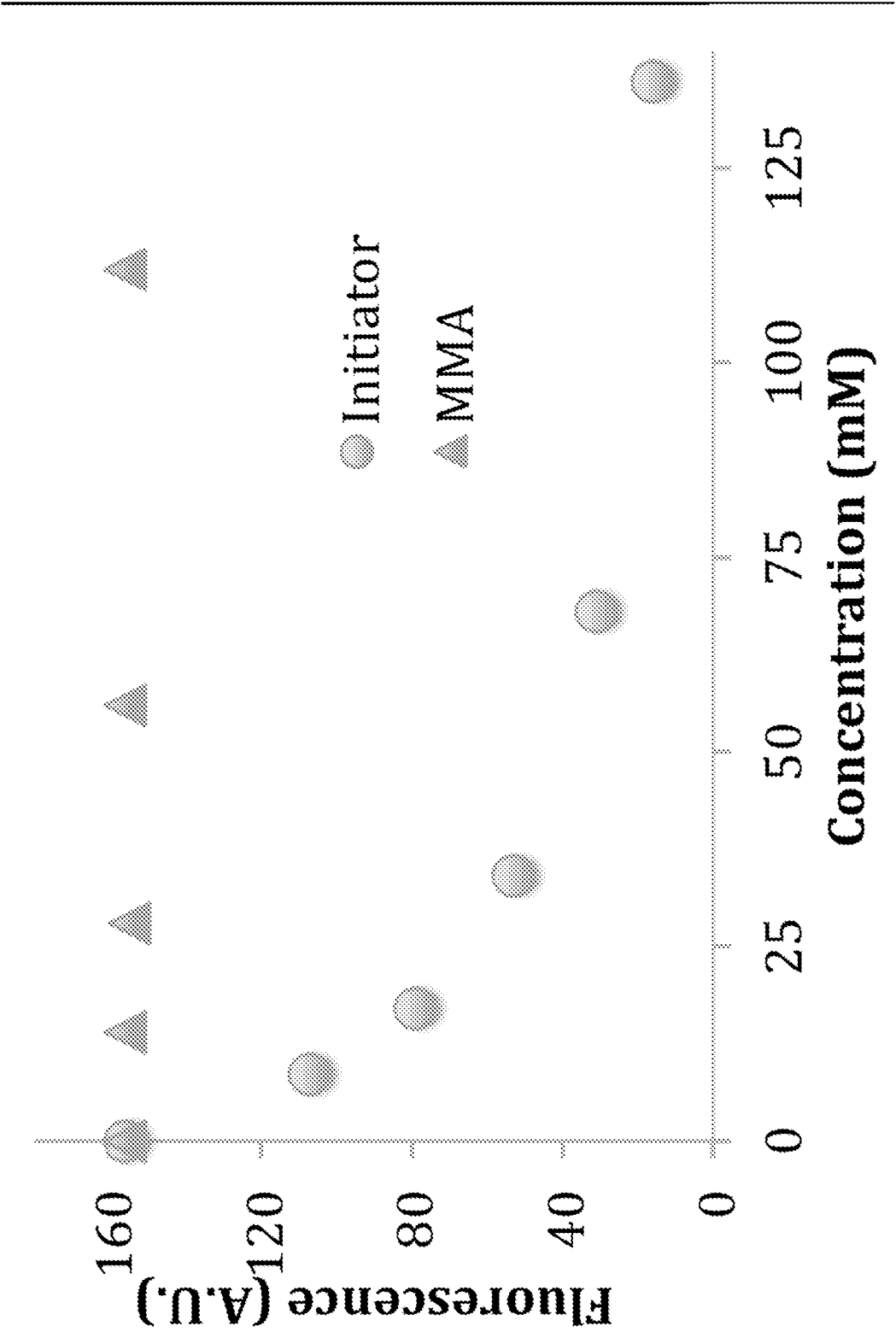
FIG. 8
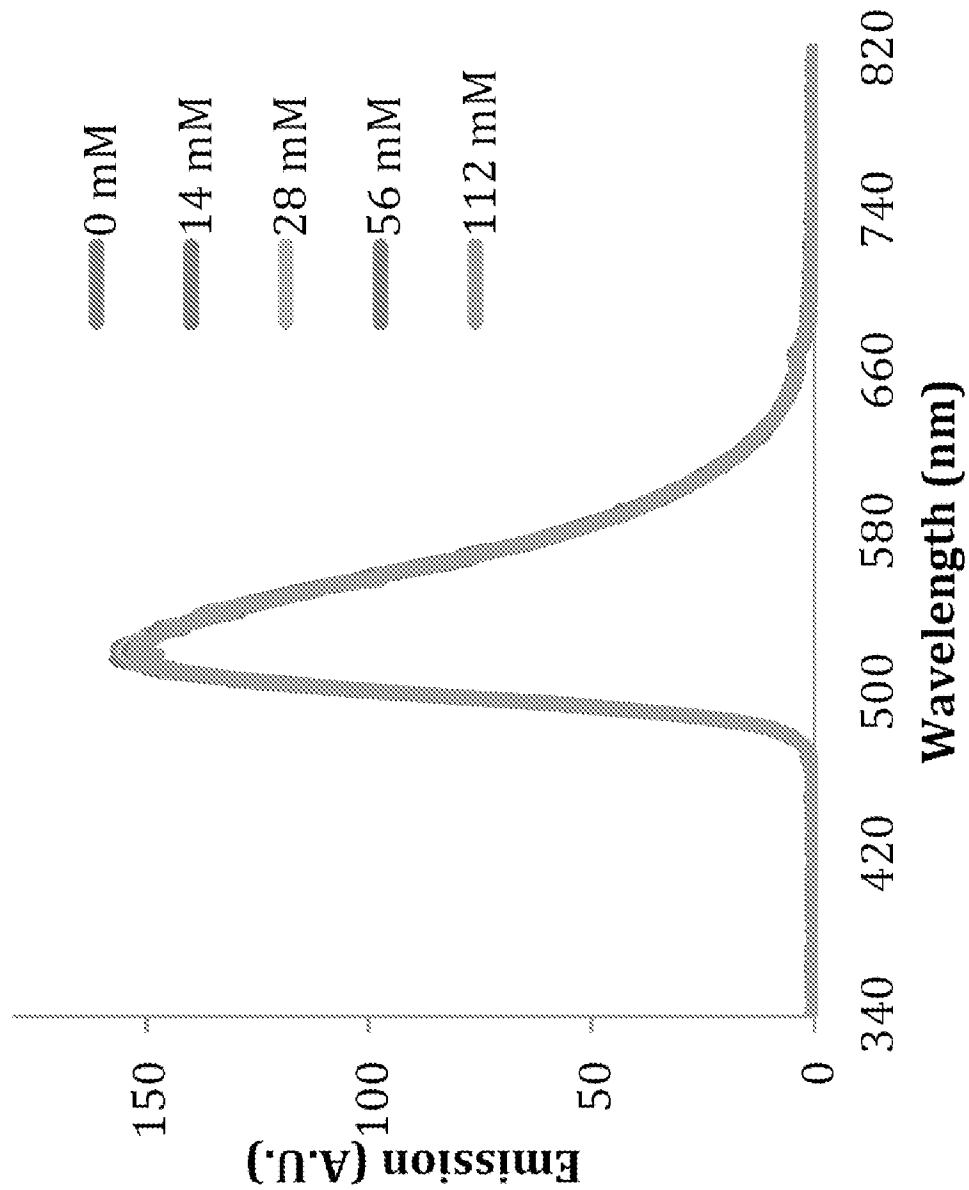
FIG. 9
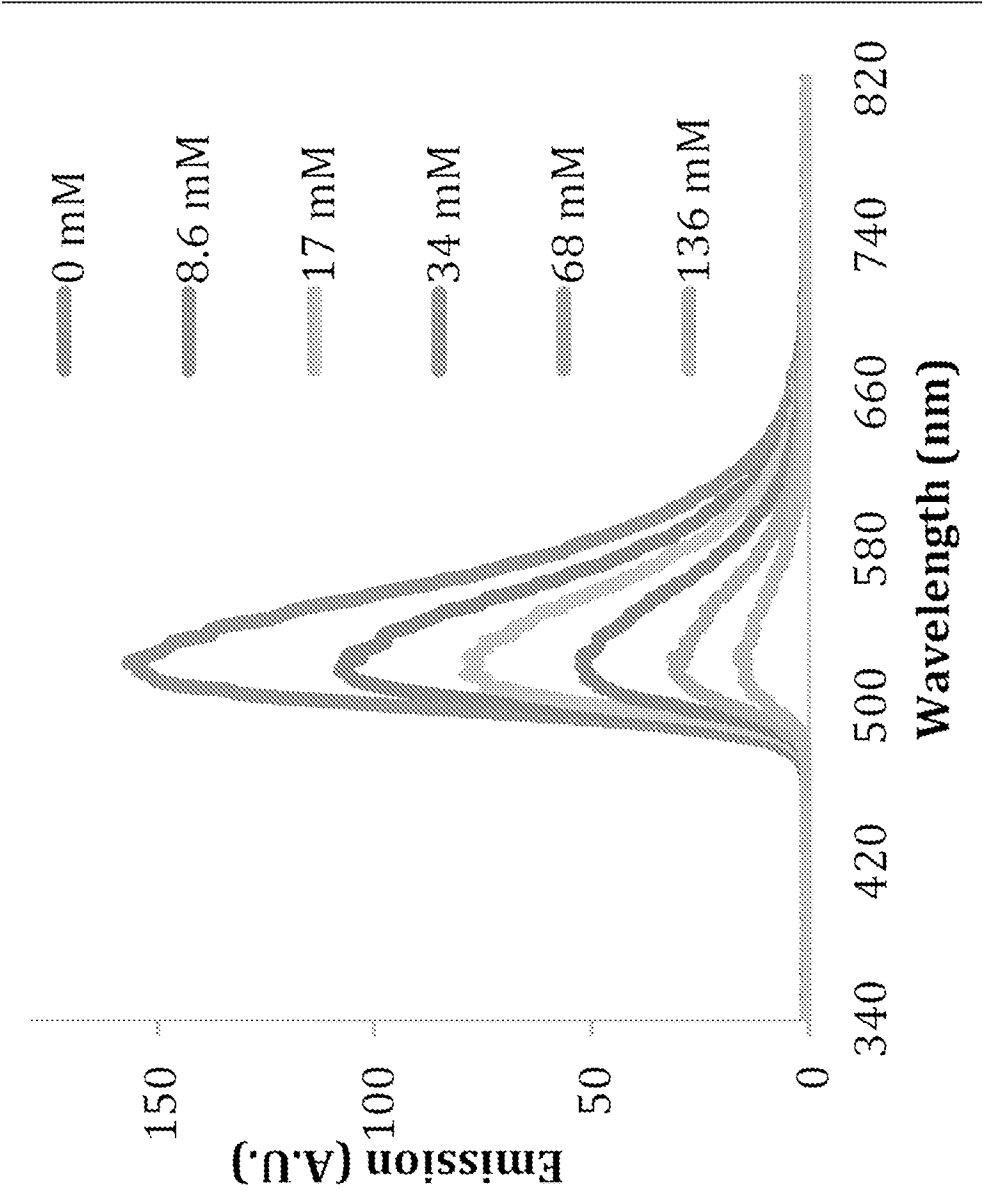
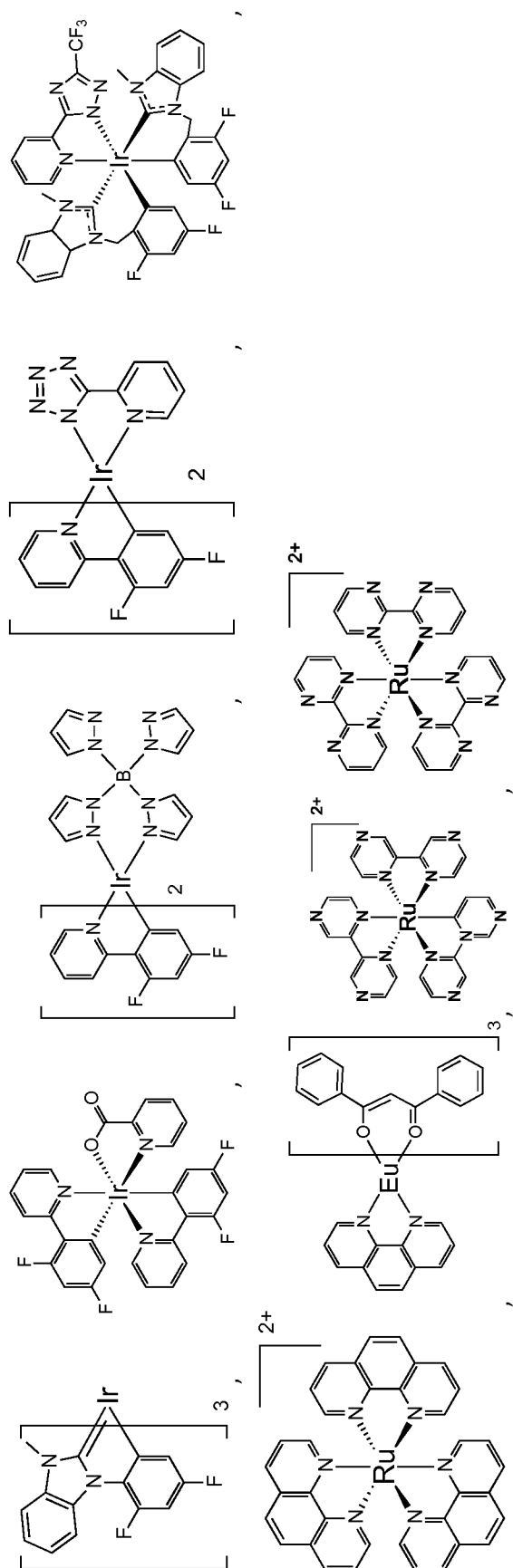FIG. 10
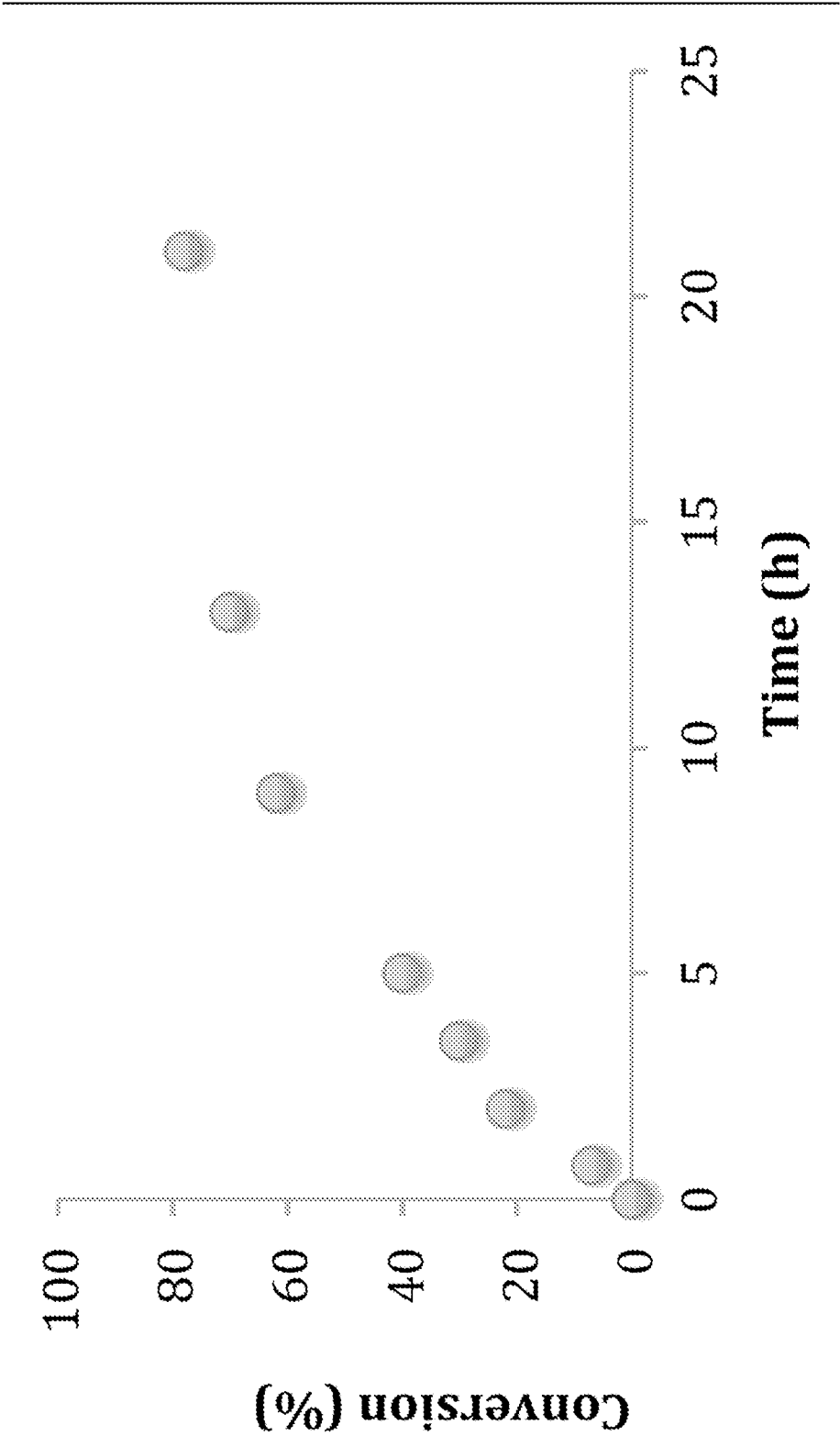
FIG. 11
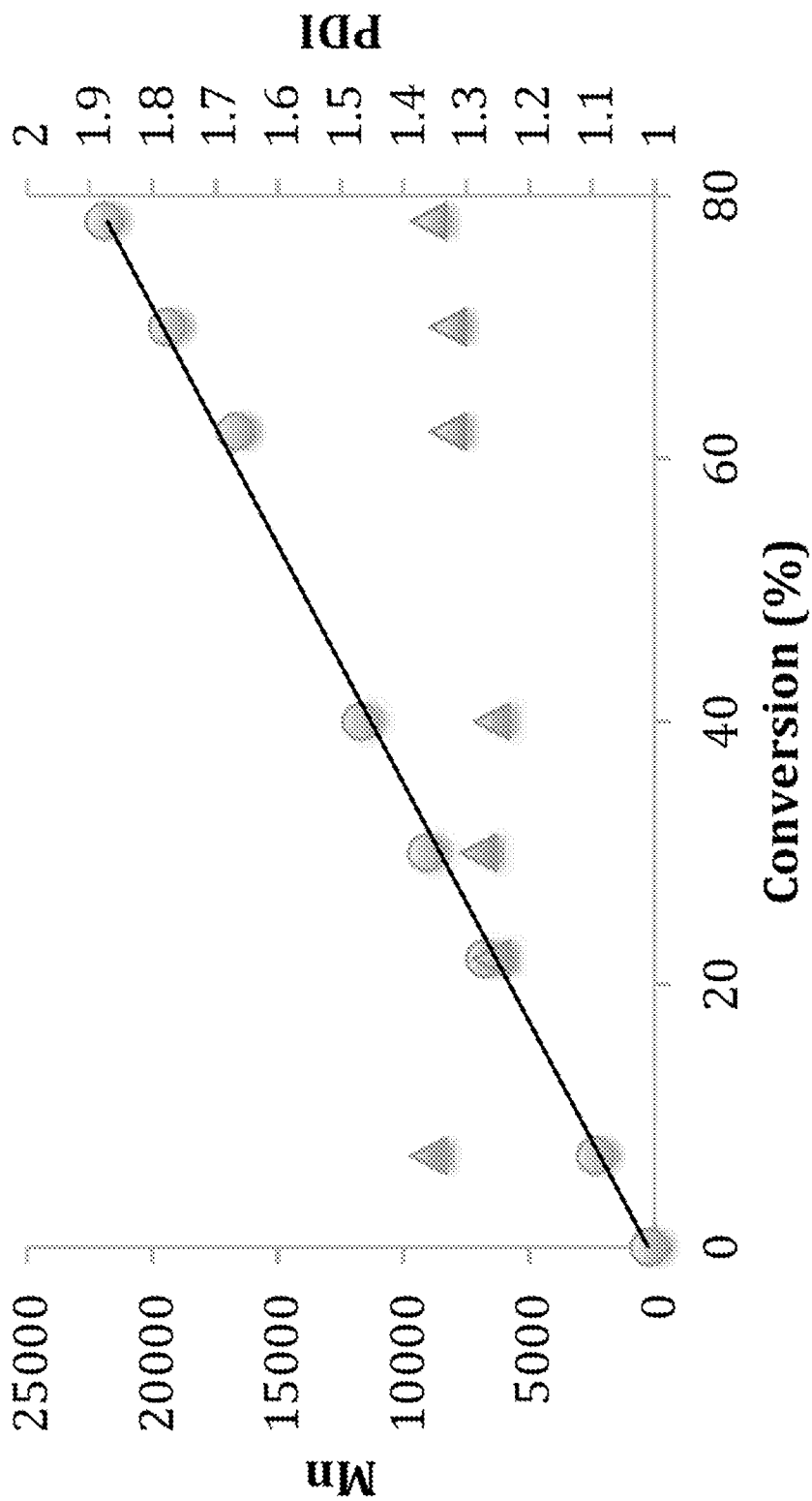
FIG. 12
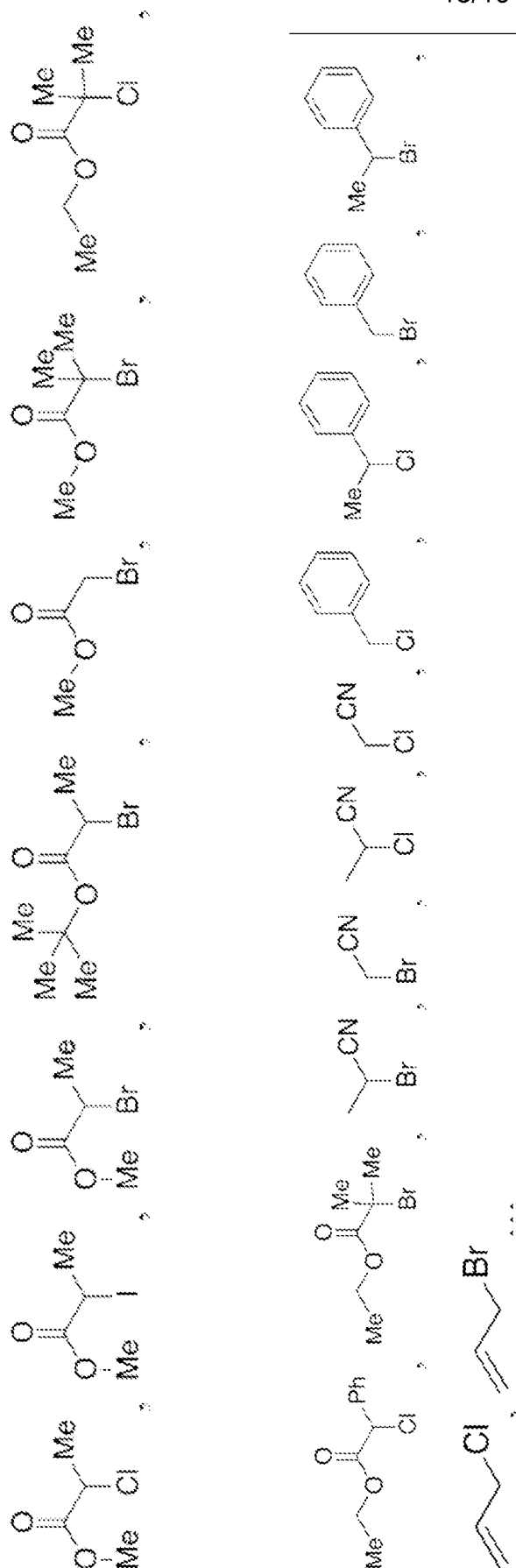
FIG. 13

FIG. 14A

FIG. 14B

FIG. 14C
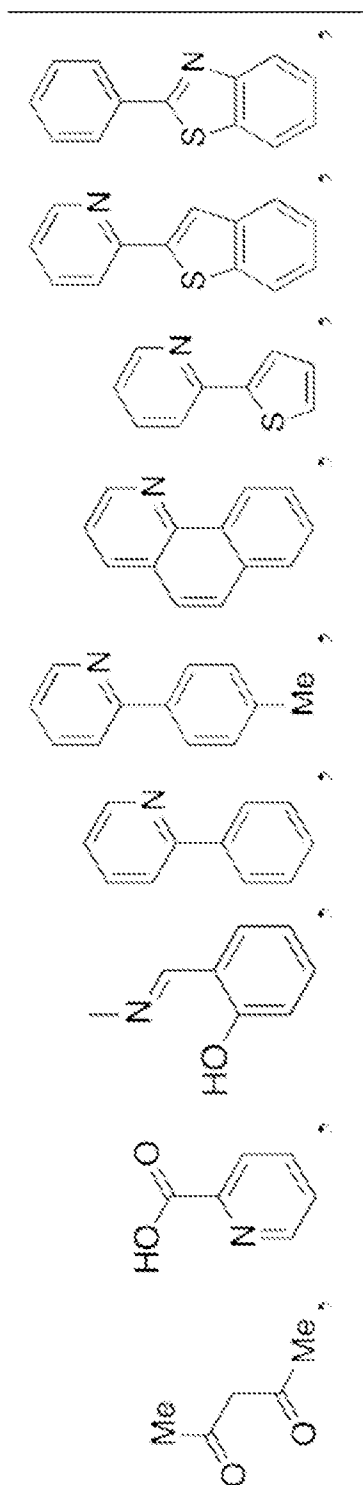
FIG. 14D
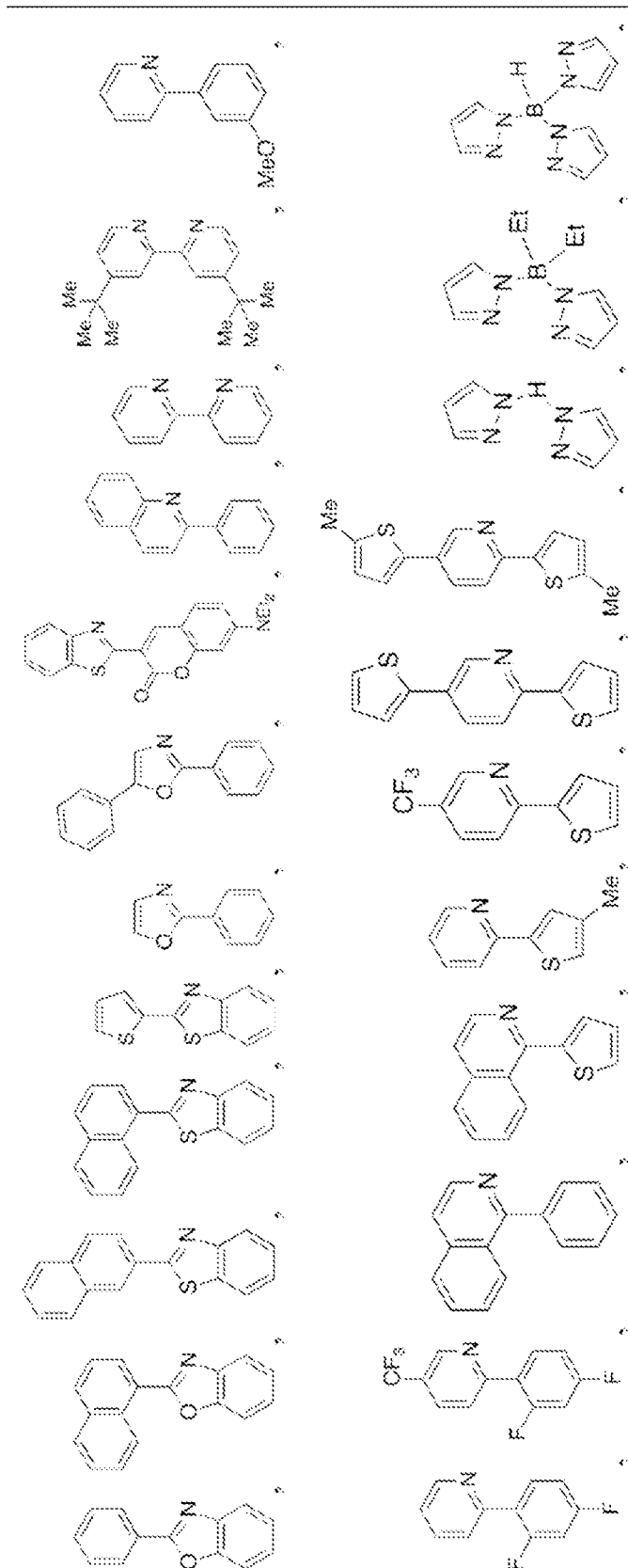
FIG. 14E
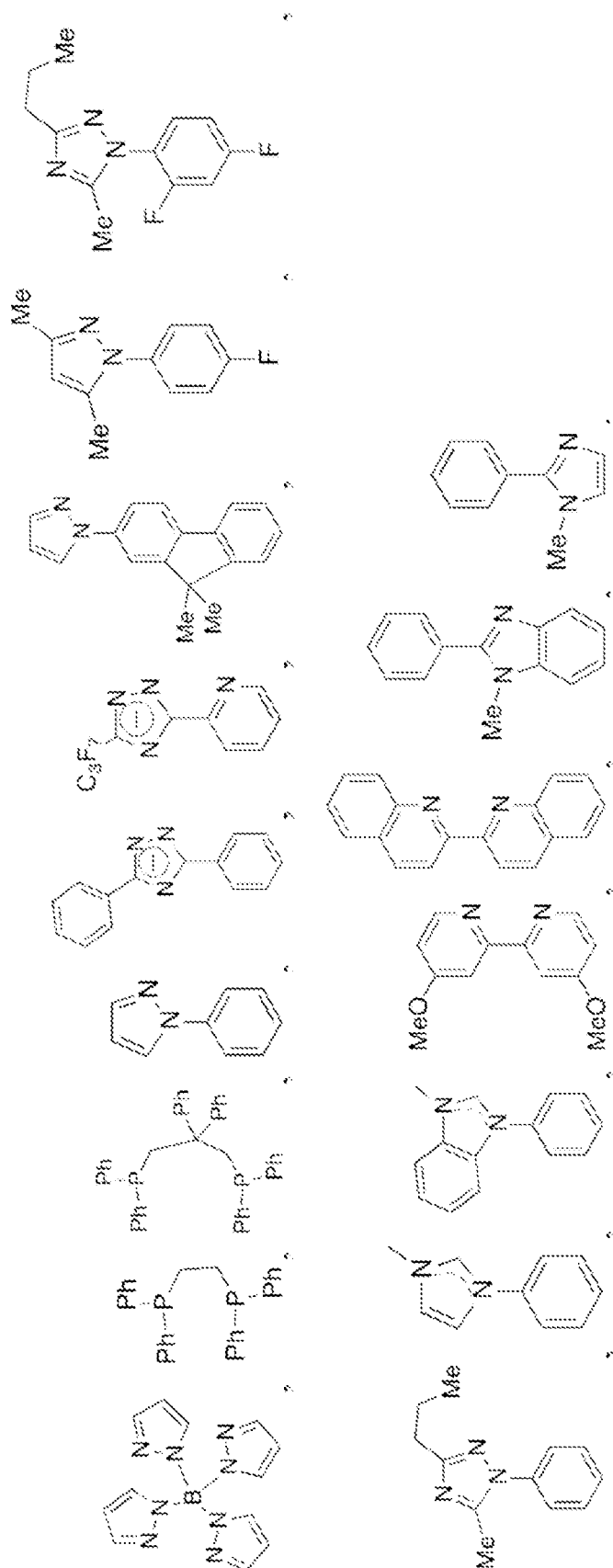
FIG. 14F

INTERNATIONAL SEARCH REPORT	International application No.
	PCT/US2013/033933

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C08F 2/48 (2013.01)
USPC - 522/6
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8) - C08F 2/00, 2/04, 2/38, 2/46, 2/48 (2013.01)
USPC - 522/4, 6; 526/72, 89, 90, 135, 136

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
CPC - C08F 2/00, 2/04, 2/38, 2/46, 2/48 (2013.01)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Orbit, Google Patents, Google Scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	ZHANG et al. Free Radical Polymerization Initiated and Controlled by Visible Light Photocatalysis at Ambient Temperature. ACS Publications. 06 September 2011. [retrieved on 23 May 2013]. Retrieved from the Internet. <URL: http://www.researchgate.net/publication/229458153_Free_radical_polymerization_initiated_and _controlled_by_visible_light_photocatalysis_at_ambient_condition/file/79e41510b207229368.pd f>. entire document	1-7, 10, 12, 13, 15-18 ------------------------------- 8, 9, 11, 14, 19, 20
Y	US 2011/0046324 A1 (MATYJASZEWSKI et al) 24 February 2011 (24.02.2011) entire document	8, 9, 19
Y	LEE et al. Spatio-Resolved, Macromolecular Architectural Surface: Highly Branched Graft Polymer via Photochemically Driven Quasiliving Polymerization Technique. American Chemical Society. 23 September 1999. [retrieved on 23 May 2013]. Retrieved from the Internet. <URL: http://pubs.acs.org/doi/abs/10.1021/ma990566b>. entire document	11, 14
Y	US 2009/0188622 A1 (BOWEN) 30 July 2009 (30.07.2009) entire document	20
Y	US 6,455,064 B1 (NARANG et al) 24 September 2002 (24.09.2002) entire document	20

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 May 2013	1 3 JUN 2013

Name and mailing address of the ISA/US	Authorized officer:
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450	Blaine R. Copenheaver
Facsimile No. 571-273-3201	PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)