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(54) Title: MOLECULE-BASED MAGNETIC POLYMERS

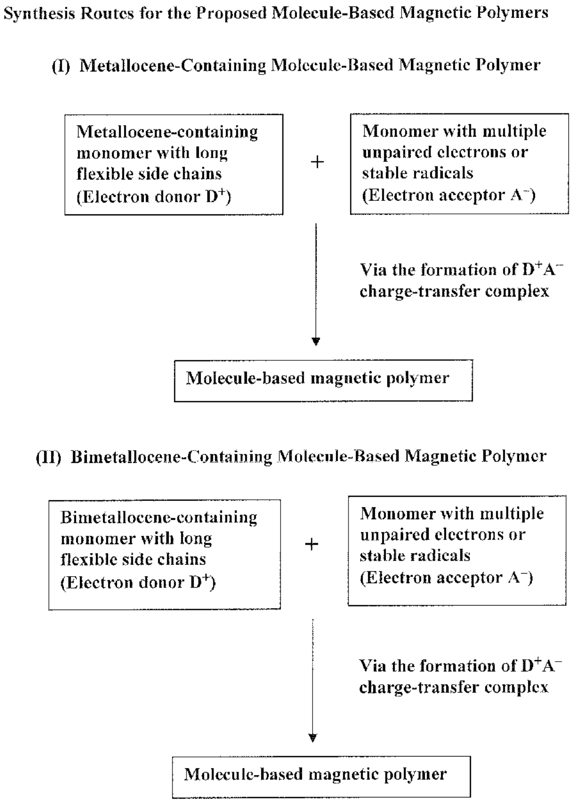

FIG. 1

(57) Abstract: Molecule-based magnetic polymers and methods of preparing are provided. In particular, a magnetic polymer having repeating units of an electron-donor metallocene-containing monomer covalently bonded to an electron-acceptor monomer having a plurality of unpaired electrons is disclosed. Also disclosed is a magnetic polymer having repeating units of an organometallic monomer covalently bonded to a stable free-radical based monomer. Homogeneous magnetorheological fluids and methods of preparing are also provided. In particular, magnetorheological fluids include a magnetic polymer in a carrier solvent.

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MOLECULE-BASED MAGNETIC POLYMERS

Cross Reference to Related Applications

This application claims priority to U.S. Provisional Application Serial No. 60/970,723 filed on September 7, 2007 and U.S. Provisional Application Serial No. 60/970,752 filed on September 7, 2007, each of which are incorporated herein by reference in their entirety.

Technical Field

The invention relates to magnetic polymers and methods of making such polymers. More particularly, the invention relates to magnetic polymers and methods of making such polymers with electron-donor metallocene compounds and electron-acceptor organic-based compounds with unpaired electrons. Magnetorheological fluids and methods of preparing are also provided. In particular, magnetorheological fluids include a magnetic polymer in a carrier solvent.

Background of the Invention

Magnets serve an indispensable function in our technology-based society and are ubiquitous in all varieties of mechanical and electronic devices in science and industry. Traditional magnets are atom-based, and are comprised of the transition, lanthanide, or actinide metals, with the magnetism arising from the magnetic dipole moment that is a product of the presence of unpaired electrons in the d- or f-orbitals.

Previous research attempts to design and synthesize molecular organic magnets and high-spin molecules with intrinsic magnetic properties were unsuccessful and very few have been found to be of industrial use, as such molecules had a fairly low ferromagnetic transition temperature, commonly referred to as Curie temperature (T_c). There remain fundamental obstacles that seem to block the ability to resolve scientific difficulties to developing organic magnets with high T_c (much higher than room temperature). There are only a few examples of organic magnets that have T_c above room temperature, but such materials are insoluble and infusible, and thus the problem of fabrication of magnetic films and liquid magnets still remains unresolved. Since the magnetic anisotropy in organometallic magnets is considerably lower than that in the case of metal-containing compounds arising from the weak spin-orbital coupling between s and p electrons, high-T_c molecular magnets have not yet been realized.

Development of molecule-based magnetic polymers would be worthwhile because they may exhibit numerous desirable properties, including solubility, processability, and synthetic tenability. Such features are a direct result of the molecular nature of molecule-based magnetic polymers and are not shared by traditional atom-based magnets. Molecule-based magnetic polymers provide prospects for new nanoscale molecular materials as functional magnetic memory devices leading to dramatically enhanced data processing speeds and storage capacity in computers or many other applications. Such polymeric magnets would be lighter, more flexible, and less intensive to manufacture than conventional metal and ceramic magnets. Applications could include magnetic shielding, magneto-optical switching, and candidates for high-density optical data storage systems.

The theory of magnetism is primarily based on two quantum mechanical concepts: electron spin and Pauli Exclusion principles. From the Curie law, the magnetic susceptibility (χ) is expressed by $\chi = N^2g\beta^2S(S + 1)/3k_BT$ where β is the effective magnetic moment, g is g-factor, N is Avogadro's number, S is the spin angular momentum, k_B is the Boltzmann constant, and T is the absolute temperature. Thus, χ is proportional to S^2 (thus high spin is required for high magnetic properties), but inversely proportional to T. Also, there is a critical temperature, T_c, below which the ferromagnetic materials exhibit spontaneous magnetization. To date, the most challenging issue for the synthesis of molecule-based magnetic polymers is to increase the T_c to well above room temperature, which desirable for industrial applications.

The conventional molecular/organic magnets used at present are all atom-based. They exist in the form of crystals or complex through noncovalent bonds (e.g., hydrogen bonding, ionic interactions, or metal coordinations), and thus spin coupling largely depends on the lattice distance of the crystal, because the exchange interaction is proportional to $1/r^{10}$. Some previous research has focused on the formation of charge-transfer (CT) complex to design and synthesize molecular/organic magnets. It has been pointed out that there are large positive and negative atomic densities in certain structures (e.g. aromatic radicals), and that atoms of positive spin density are exchange coupled most strongly to atoms of negative spin density in neighboring molecules. The delocalization of spin density in macromolecular chains makes it possible for magnetic interactions to take place across extended bridges between magnetic centers far apart from each other, propagating through conjugated bond linkages, which act as molecular wires. Spin polarization, i.e., the simultaneous existence of positive and negative spin densities at different locations within a given radical is crucial for intermolecular exchange interactions to bring about ferromagnetic interactions. Employing iron or transition metal with larger radial orbitals as magnetic centers will improve the overlap between the orbitals of electron acceptor (A^-) and electron donor (D^+), namely spin coupling. Currently, there have been no successful attempts reported on the synthesis of molecule-based magnetic polymers forming CT complex.

Magnetic polymers based on p-orbital spins typically exhibit weak ferromagnetic properties and thus T_c is still below 10 K even when S reaches 5000. Therefore, it is necessary to incorporate much stronger magnetic centers into the macromolecular chains, such as iron or other transition metals having the unpaired electrons located in d- or f-orbitals.

Existing superparamagnetic nanocomposites typically contain magnetic particles (e.g., Fe, Co, Ni etc.) in the form of powder or flakes in a non-magnetic polymer matrix. Due to the tendency of aggregation of magnetic particles when added to a non-magnetic polymer matrix, the magnetic particles were typically treated with a surfactant or another polymer in order to help suppress aggregation. Owing to a much higher density of magnetic particles compared with that of non-metallic polymer matrix, the magnetic particles had a tendency to settle out at rest or during storage. Consequently, non-uniform dispersion of magnetic particles in the polymer matrix and poor heat dissipation during use represent additional problems.

The volume fraction of the magnetic particles in superparamagnetic nanocomposites is much smaller than that of the matrix polymer, and therefore the resulting magnetic level is not high. Thus, applications of superparamagnetic nanocomposites are limited.

Further limitations of superparamagnetic nanocomposites include the lack of solubility in common solvents which prevents them from being used in the preparation of magneto-rheological (MR) fluids. Thus, magnetic particles (e.g., iron oxide or ferrite) are suspended in a carrier liquid to prepare MR fluids and they are used in industry (e.g., in automotive industry). Conventional MR fluids suffer from the same problem as superparamagnetic nanocomposites in that the magnetic particles tend to aggregate and also sediment at rest.

MR fluids currently in use are typically suspensions containing magnetic particles (iron oxide or ferrite for example) with typical volume fractions of 0.3–0.4 in a carrier fluid (typically silicone oil). The conventional, commercially available MR fluids also typically contain an organic additive in order to stabilize the dispersion of aggregates of magnetic particles. Due to the large difference in density between the magnetic particles (having a density of 5–6 g/cm^3)

and a carrier fluid (having a density less than 1 g/cm^3), the conventional MR fluids have serious technical problems. In particular, the magnetic particles in the conventional MR fluids settle out over a relatively short period of time (i.e., in a few minutes to a few hours). Another technical difficulty is related to the lack of redispersibility of the magnetic particles in the conventional MR fluids. After the magnetic particles settle, they form highly dense aggregates, the extent of which depends on the chemical structure of a carrier fluid. To help disperse the aggregates of magnetic particles in a heterogeneous MR fluid, considerable efforts have been spent on treating the particles with a surfactant or a polymeric gel during the preparation of such MR fluids.

Notwithstanding the state of the art as described herein, there is a need for further improvements in molecule-based magnetic polymers. Furthermore, there is a need for further improvements in molecule-based (i.e. homogeneous) magnetic polymers. These types of polymers (without the presence of magnetic nanoparticles) would have numerous applications and would enable the preparation of homogeneous MR fluids without the need for magnetic particles, which can then replace conventional MR fluids that have inherent difficulties of sedimentation and aggregation of magnetic particles.

Summary of the Invention

In one embodiment of the invention, molecule-based magnetic polymers and methods of preparing these compounds are disclosed. In a further embodiment of the invention, a series of monomers are prepared having the properties of (1) either having multiple unpaired electrons ("spins") and thus play the role of electron acceptor resulting in the formation of CT complex with an electron donor or (2) forming stable radicals (e.g., verdazyl radicals) and thus have reactions with at least one transition metal, for example iron, cobalt, or nickel that is located within a ferrocene-, cobaltocene-, or nickelocene-containing and biferrocene-, bicobaltocene-, or binickelocene-containing monomer, with long flexible side chains resulting in the formation of metal-verdazyl coordination complex. The two monomers can then be polymerized to obtain covalently linked molecule-based magnetic polymers. The synthesized polymers are soluble in organic solvents, since they will have long flexible, hydrophobic side chains.

In another embodiment of the invention, a magnetic polymer having repeating units of a metallocene-containing electron-donor monomer covalently bonded to a monomer having a plurality of unpaired electrons is disclosed. Such polymers can be synthesized by covalent bonding, for instance, between a metallocene-containing electron-donor monomer and an electron-acceptor organic-based monomer with unpaired electrons.

In yet another embodiment of the invention, a magnetic polymer having repeating units of a metallocene-containing electron-donor monomer covalently bonded to a free-radical based monomer is disclosed.

In a further embodiment of the invention, a method of preparing a magnetic polymer is disclosed. The method includes the steps of preparing a metallocene-containing electron-donor monomer, preparing a monomer having a plurality of unpaired electrons, and polymerizing the metallocene-containing electron-donor monomer and monomer having a plurality of unpaired electrons to form a magnetic polymer.

In yet another embodiment of the invention, a method of preparing a magnetic polymer is disclosed. The method includes the steps of preparing an organometallic monomer, preparing a free-radical based monomer and polymerizing the organometallic monomer and free-radical based monomer to form a magnetic polymer.

In still yet another embodiment of the invention, a magnetorheological (MR) fluid includes a carrier solvent, and a magnetic polymer soluble in the carrier solvent, wherein the magnetic polymer comprises repeating units of an organometallic monomer covalently bonded to a monomer having a plurality of unpaired electrons.

In a further embodiment of the invention, a magnetorheological fluid includes a carrier solvent, and a magnetic polymer soluble in the carrier solvent, wherein the magnetic polymer comprises repeating units of an electron-donor metallocene-containing monomer covalently bonded to a stable free-radical based monomer.

In still yet a further embodiment of the invention, a method of preparing a magnetorheological fluid includes the steps of preparing a magnetic polymer including the steps of preparing an electron-donor metallocene-containing monomer, preparing a monomer having a plurality of unpaired electrons, and polymerizing the electron-donor metallocene-containing monomer and monomer having a plurality of unpaired electrons to form the magnetic polymer, and mixing the magnetic polymer with a carrier solvent.

In another embodiment of the invention, a method of preparing a magnetorheological fluid includes the steps of preparing a magnetic polymer comprising the steps of preparing an electron-donor metallocene-containing monomer, preparing a preparing a stable free-radical based monomer, and polymerizing the electron-donor metallocene-containing monomer and the stable free-radical based monomer to form the magnetic polymer, and mixing the magnetic polymer with a carrier solvent.

Brief Description of the Drawings

FIG. 1 is a schematic representation of proposed synthesis routes for molecule-based magnetic polymers;

FIG. 2a is graph representing the X-ray diffraction (XRD) pattern of a molecule-based polymer P5 measuring intensity versus two-theta angle;

FIG. 2b is graph representing the X-ray diffraction (XRD) pattern of iron oxide measuring intensity versus two-theta angle;

FIG. 3 is graph representing the electron spin resonance (ESR) spectrum of a molecule-based polymer P5;

FIG. 4a is a photograph showing homogeneous magnetic solution of a molecule-based polymer P5 in a solvent at 0.1 wt%;

FIG. 4b is a photograph showing homogeneous magnetic solution of a molecule-based polymer P5 in a solvent at 1.0 wt%; and

FIG. 4c is a photograph showing homogeneous magnetic solution of a molecule-based polymer P5 in a solvent at 10.0 wt%.

Detailed Description of the Invention

The synthesis procedures for a series of high-T_c molecule-based magnetic polymers and the presentation of representative properties of the synthesized magnetic polymers are presented herein. These molecule-based magnetic polymers are soluble in common solvents, offering good processability. The term “molecule-based”, as used herein, refers to the state of covalent bonding between elements and/or atoms during the formation of large molecules, i.e. polymers. The molecule-based magnetic polymers, as described herein, are intrinsically homogeneous in nature.

The design and synthesis of molecule-based magnetic polymers may be based on the following theoretical considerations. Namely, (a) the macromolecular chains must have magnetic centers with unpaired electrons, (b) the unpaired electrons should have their spins aligned parallel along a given direction, (c) conjugated structure plays an important role in intramolecular spin coupling along the macromolecular chain, and (d) spin coupling must extend to three dimensions, due to the cooperative effect of magnetism, which can be realized from the spin delocalization and spin polarization along the macromolecular chains, and intermolecular exchange interactions.

These molecule-based magnetic polymers allow creation of ferromagnetic materials having numerous practical applications. These applications include diagnostics, bioassays and life sciences research, as they may provide a means of separation of substances from complex mixtures. For example, a ligand (e.g., antibody or antigen), may be either non-covalently or covalently attached to the magnetic particle through chemical means. Other applications include exclusion seals for computer disc drives, applications such as seals for bearings, for pressure and vacuum sealing devices, for heat transfer and damping fluids in audio speaker devices. Further applications include magnetic toner and inkjet formulations. Further, the magnetic polymers can be used to prepare homogeneous magnetorheological fluids (MR) for numerous automotive or other applications.

MR fluids are used in many different applications. For instance, in the automotive industry, MR fluids are used for electrically controllable shock absorbers, clutches, inertial damper, actuators, and engine mounts. The reason for the use of MR fluids in such applications lies in that an applied magnetic field induces an orientation of magnetic particles (in the conventional MR fluids) along the direction of magnetic field, giving rise to a very high resistance to flow, often referred to as "yield stress." Field-induced yield stress is a very unique characteristic of MR fluids. The rheological properties of MR fluids such as viscosity, yield stress, and stiffness can be altered by an external magnetic field. The unique features of these changes are fast (on the order of milliseconds), significant, and nearly completely reversible. Specifically, in the "off" state (when no magnetic field is applied), the magnetic centers are randomly distributed, and thus the MR fluid behaves like a Newtonian fluid, whereas, in the "on" state (when a magnetic field is applied), the magnetic centers form columns, chains, or more complex structures aligned with the field direction, which causes the MR fluid to exhibit semisolid behavior with increased yield stress, characteristic of Bingham fluids. The viscosity of MR fluids is dependent on the magnitude and direction of the applied magnetic field as well as the shear rate. For example, field-induced yield stress will help a driver to stop a car quickly.

The invention therefore is directed to molecule-based magnetic polymers, and homogeneous molecule-based magnetic polymers, with such polymers usable as polymers and in MR fluids or the like. The term "homogeneous", as used herein, refers to a "single phase" state in which substantially no free magnetic particles or extraneous foreign particles exist in the synthesized magnetic polymer product in the bulk state, for solids, or in the liquid state, for fluids.

Previous attempts to synthesize molecule-based magnetic polymers were unsuccessful. In the present invention, theoretical considerations were used to develop the synthesis of the chemical structures from monomers that enhance spin-spin interactions between the constituent components, which then leads to molecule-based magnetic polymers after polymerization. It was considered previously that the synthesis of molecule-based magnetic polymers with high T_c would not be possible without using a monomer having a metallic element (e.g., iron. cobalt, or nickel).

Thus, as an embodiment of the invention a series of monomers have been synthesized having (1) either multiple unpaired electrons ("spins") and thus play the role of electron acceptor resulting in the formation of charge-transfer complex (CT) with an electron donor or (2) stable free radicals (e.g., verdazyl radicals) and thus have reactions with at least one transition metal-containing organometallic compound, for example a metallocene, that includes iron, cobalt, or nickel in ferrocene-, cobaltocene-, or nickelocene-containing or biferrocene-, bicobaltocene-, binickelocene-containing monomer with long flexible side chains resulting in the formation of metal-verdazyl coordination complex. The two monomers were then polymerized to obtain covalently linked molecule-based magnetic polymers. The synthesized polymers may be soluble in carrier fluids or solvents, because of the properties of the long flexible side chains. In an embodiment of the invention, synthesis routes for molecule-based magnetic polymers are shown in FIG. 1.

In one embodiment of the invention, the long flexible side chains are saturated or unsaturated aliphatic, alkyl side chains having the structure:

$-(CH_2)_mCH_3$, wherein $m = 1\text{-}15$

In another embodiment of the invention, the long flexible side chains are saturated alkoxy, aliphatic alcohol, and cationic side chains having the structure:

$-CH_2CH_2O-(CH_2CH_2O)_m-CH_3$, wherein $m = 1\text{-}15$;

$-(CH_2)_m-CH(OH)_2$, wherein m = 1-15; or

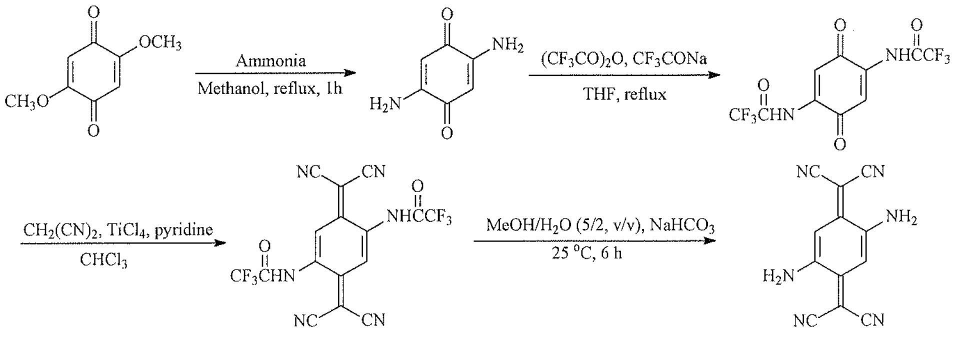
$-(CH_2)_m-N^+(CH_3)_3$, wherein m = 1-15.

In one embodiment, a suitable candidate for the carrier fluid or solvent for the magnetic polymers include, but are not limited to, an organic fluid, or an oil-based fluid. Suitable carrier fluids which may be used include natural fatty oils, mineral oils, polyphenylethers, dibasic acid esters, neopentylpolyol esters, phosphate esters, synthetic cycloparaffins and synthetic paraffins, unsaturated hydrocarbon oils, monobasic acid esters, glycol esters and ethers, silicate esters, silicone oils, silicone copolymers, synthetic hydrocarbons, perfluorinated polyethers and esters and halogenated hydrocarbons, and mixtures or blends thereof. Hydrocarbons, such as mineral oils, paraffins, cycloparaffins (also known as naphthenic oils) and synthetic hydrocarbons are one of the classes of carrier fluids. In certain embodiments, aqueous based fluids are contemplated as carrier fluids or solvents for the magnetic polymers. In one embodiment, the carrier fluid comprises substantially all one fluid. In another embodiment, the carrier fluid is a mixture of one or more carrier fluids. In one embodiment, the carrier fluid comprises an aliphatic hydrocarbon.

The magnetic properties of organic metallocene-based polymers would be highly dependent upon the chemical nature of the bridge linking the metallocenium units. With this understanding, the following monomers were synthesized for electron acceptor functionality.

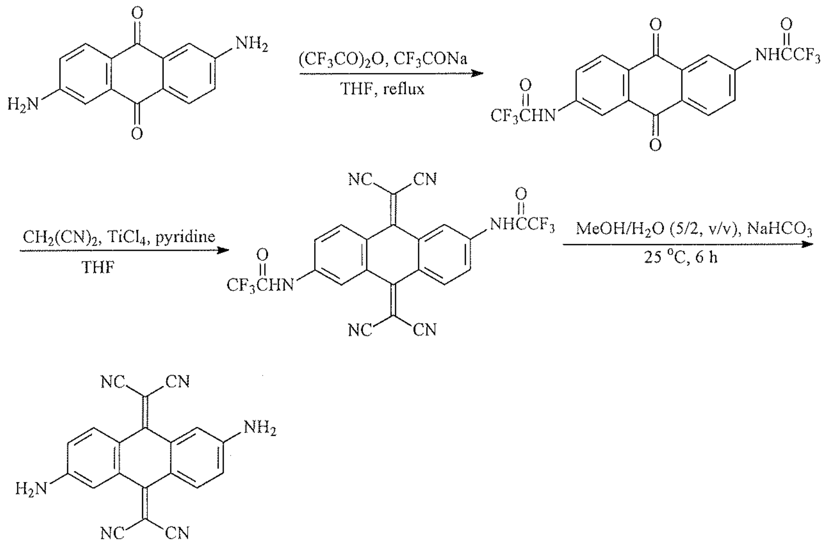
Synthesis of Five Monomers with Multiple Unpaired Electrons

1. Synthesis of Tetracyanoquinodiamine (TCNQ-DA)



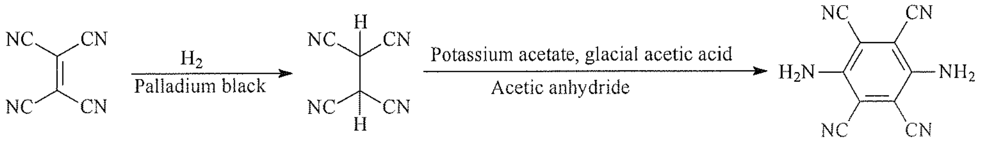
I

2. Synthesis of Tetracyanoanthraquinodiamine (TCNAQ-DA)



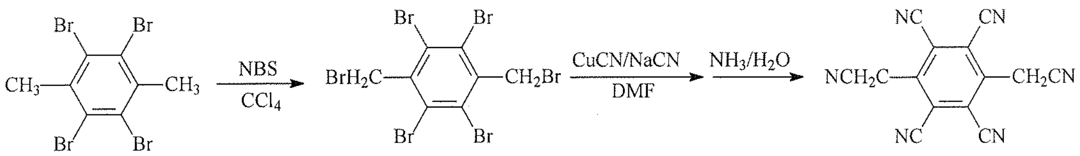
II

3. Synthesis of Tetracyano-p-phenylenediamine (TCP-DA)



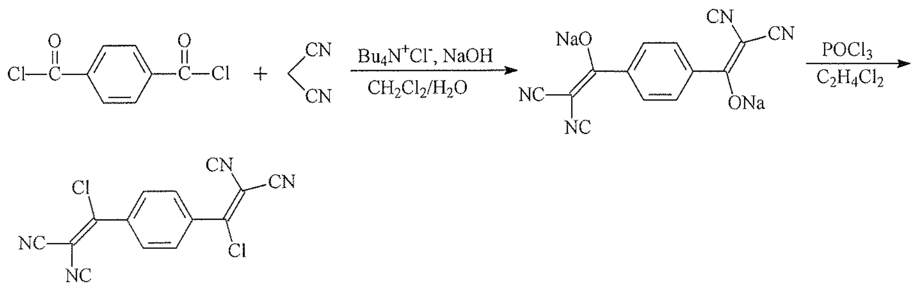
III

4. Synthesis of 1,2,4,5-Tetracyano-3,6-bis-cyanomethyl-benzene (TCCB)



IV

5. Synthesis of 1,4-Bis(1-chloro-2,2-dicyanovinyl)benzene (BCVB-DC)

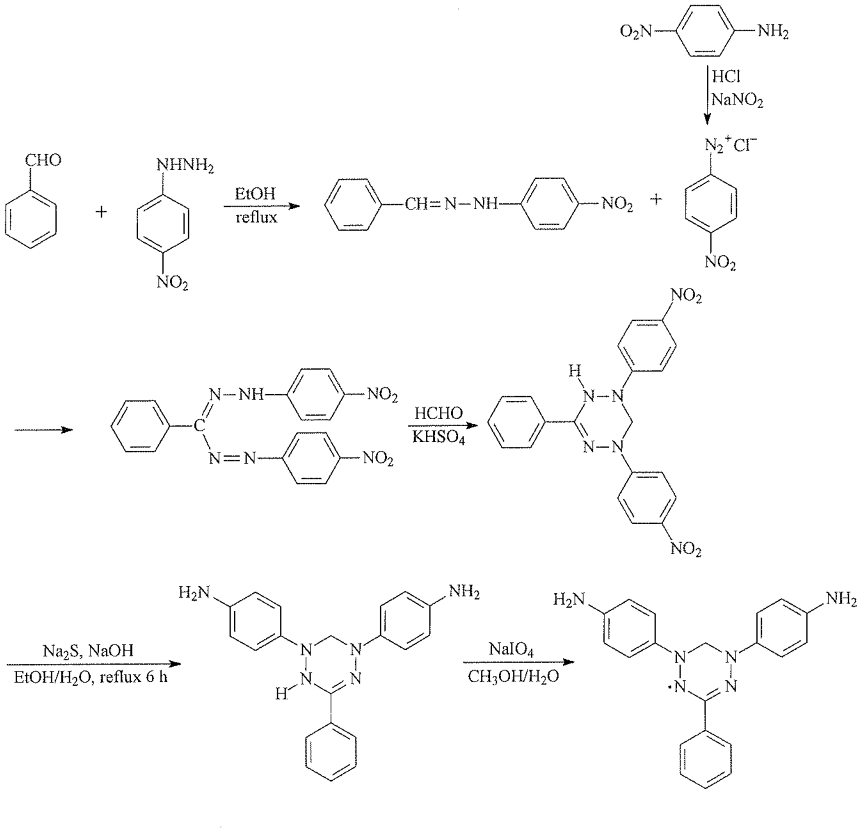


V

All these five monomers have electron-accepting units such as tetracyano and dicyano, which are known to form charge transfer (CT) complexes with an electron-donor component. Specifically, monomers **I, II, III, and IV** with tetracyano unit can polymerize with monomers containing dicarbaldehyde through their diamine groups. Monomer **V** possesses bis(dicyano) units, which can be used for preparing poly(enaminonitriles).

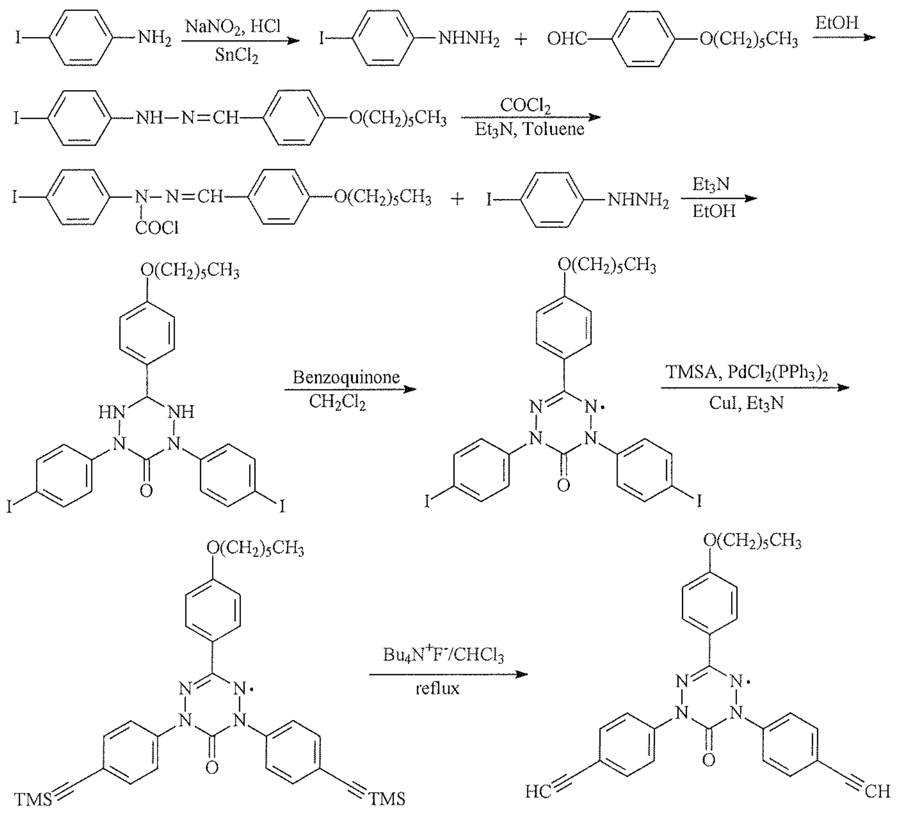
Synthesis of Four Proposed Monomers with Stable Radicals

1. Synthesis of Verdazyl-type Diamine Radical (VD-DR)



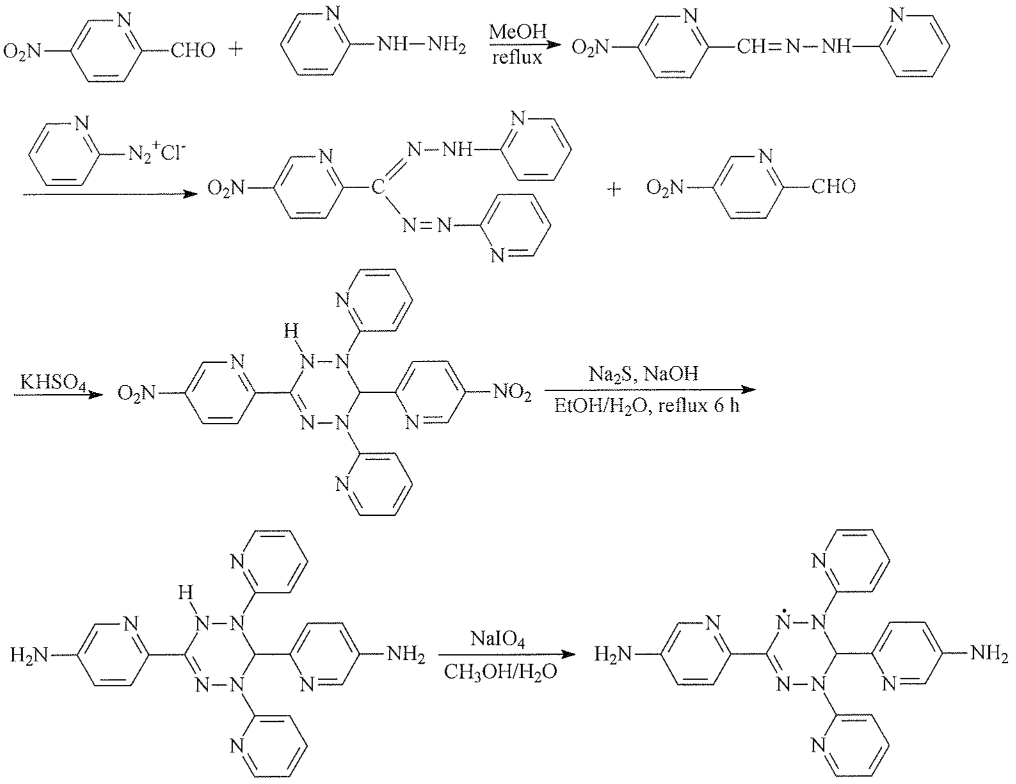
VI

2. Synthesis of Verdazyl-type Diethynyl Radical (VD-DE)



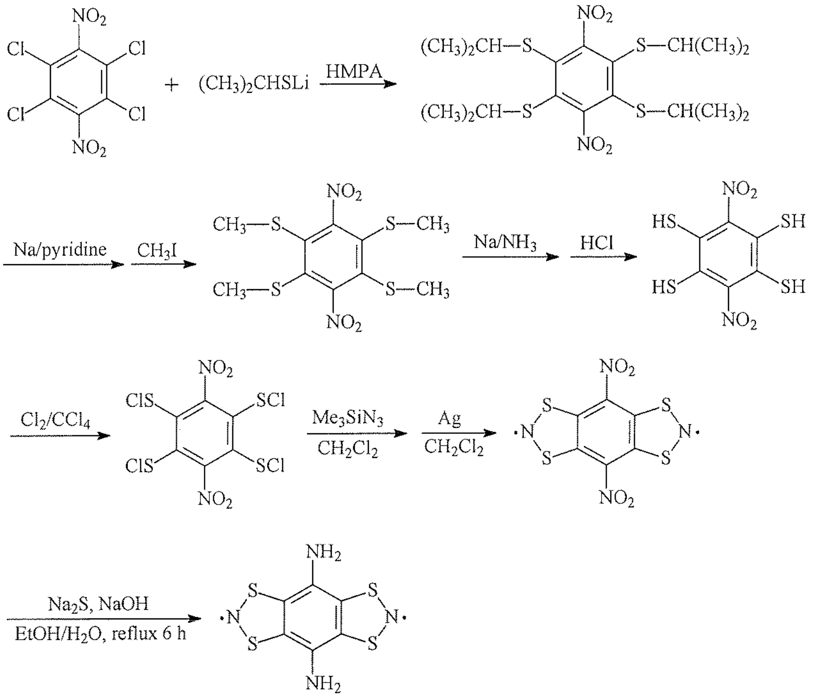
VII

3. Synthesis of Verdazyl-pyridyl-type Diamine Radical (VP-DR)



VIII

4. Synthesis of Thioaminyl Radical (T-R)



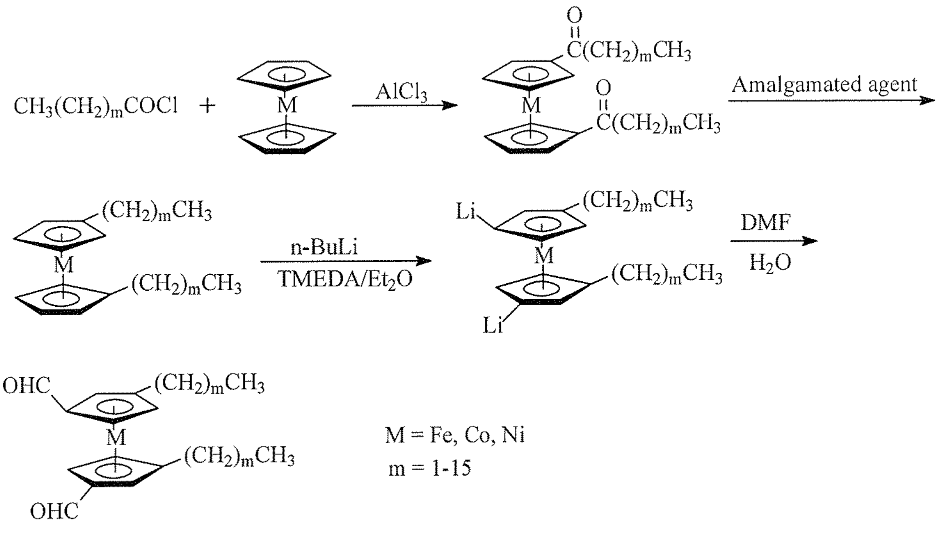
IX

Monomers **VI** and **VII** contain verdazyl-type radicals, which are known to be stable such that they can be stored for extended periods of time without decomposition. The delocalization of the unpaired electrons in verdazyl radicals is expected to result in strong magnetic interactions, i.e., through intermolecular ferromagnetic exchange interactions. Further, verdazyl radicals can readily form a coordination complex with a transition metal in a metallocene molecule. In details, monomer **VI** with diamine functional groups can react with a metallocene having dicarbaldehyde, while monomer **VII** with diethynyl functional groups can polymerize with diiodometallocene monomers. The rationale behind introducing pyridyl group in monomer **VIII** lies in the fact that it is possible to have stable pyridinyl radicals or charge-transfer pyridium structures. Monomer **IX** has a thioaminyl radical that contains oxygen-insensitive isolable thioaminyl cyclic radicals, which have an extensively delocalized π-spin system and are expected to have strong magnetic interactions with magnetic centers (e.g. iron in ferrocene).

Synthesis of Metallocene Monomers Containing a Transition Metal for Electron Donor

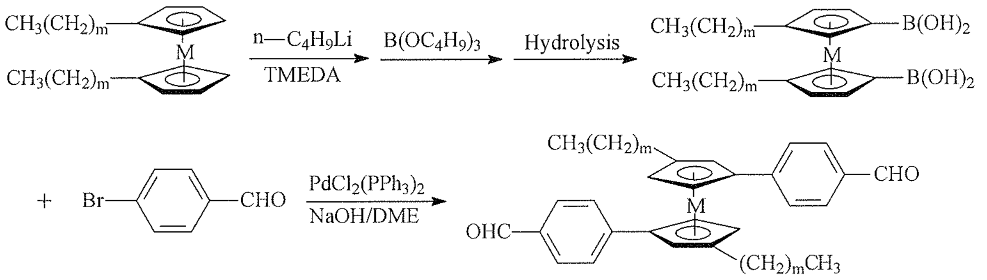
1. Synthesis of Metallocene Monomers with Long Flexible Side Chain

One of the existing problems that must be overcome to synthesize a truly molecule-based magnetic polymer is the solubility of the polymer in commercially available solvents. In one embodiment of the invention, a metallocenedicarbaldehyde monomer with long flexible side chains was prepared. Previous research showed that a ferromagnetic polymer synthesized without long flexible side chains was not soluble in organic solvents. Therefore, when a magnetic polymer is not soluble in a solvent, its practical use is very limited in that the fabrication of many useful industrial products would not be possible. Thus, metallocenes (including ferrocene, cobaltocene, and nickelocene) were chemically modified with dialdehyde group and long alkyl side chains yielding the chemical structure **X**:



X

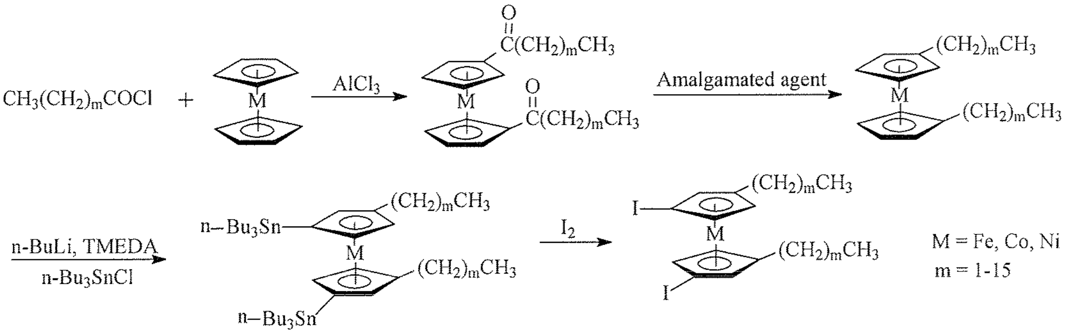
In order to obtain polymers with high molecular weights, we have made some modification of monomer **X** through incorporating phenyl unit between ferrocene and aldehyde functional group yielding the chemical structure **XI**:



M = Fe, Co, Ni
m = 1-15

XI

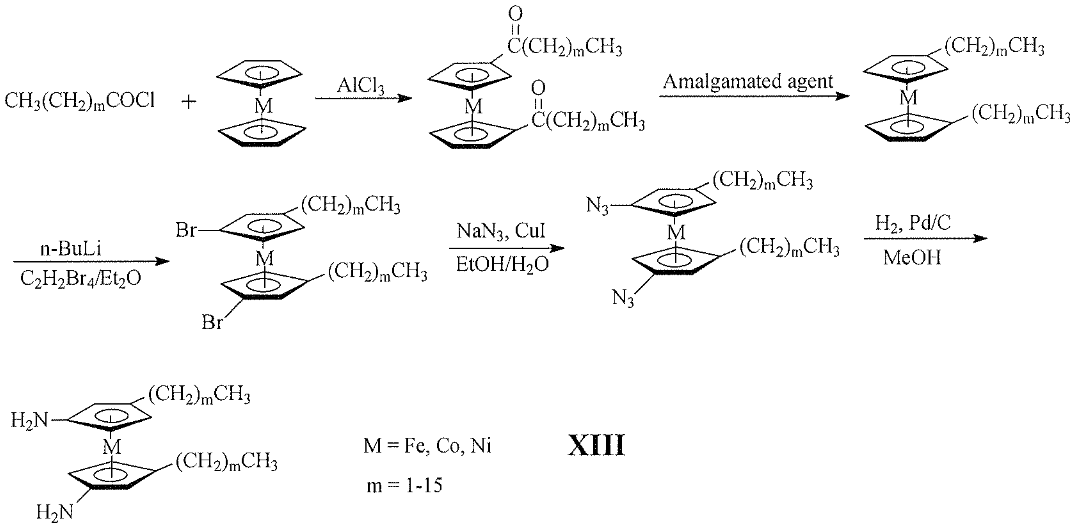
Similarly, monomer **XII** diiodometallocene having long flexible side chains was also synthesized:



M = Fe, Co, Ni
m = 1-15

XII

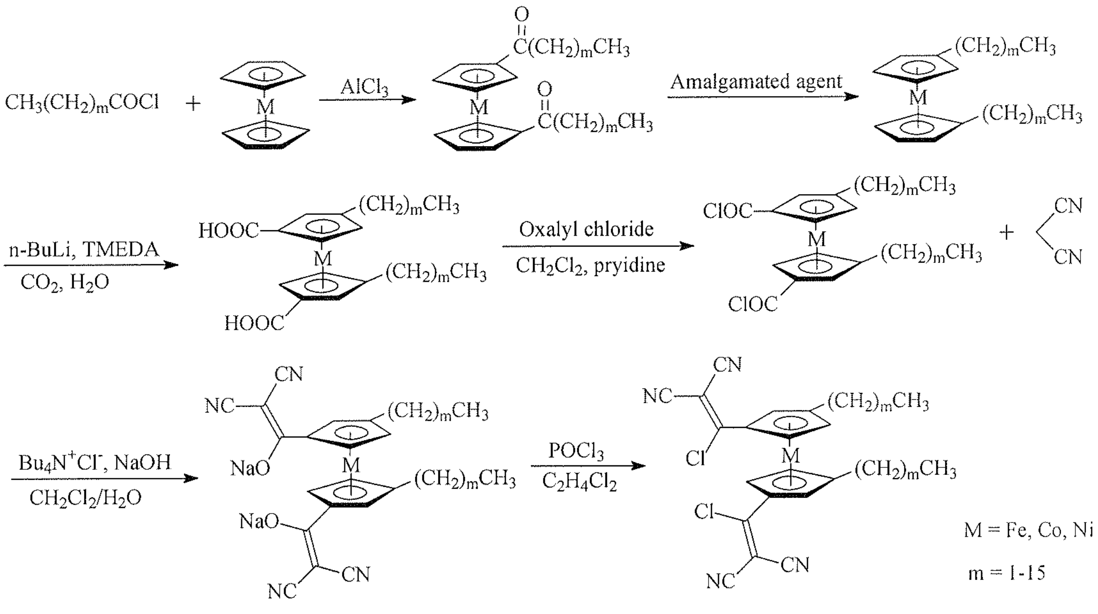
Another metallocene monomer **XIII** having long flexible side chains was functionalized with diamine:



M = Fe, Co, Ni
m = 1-15

XIII

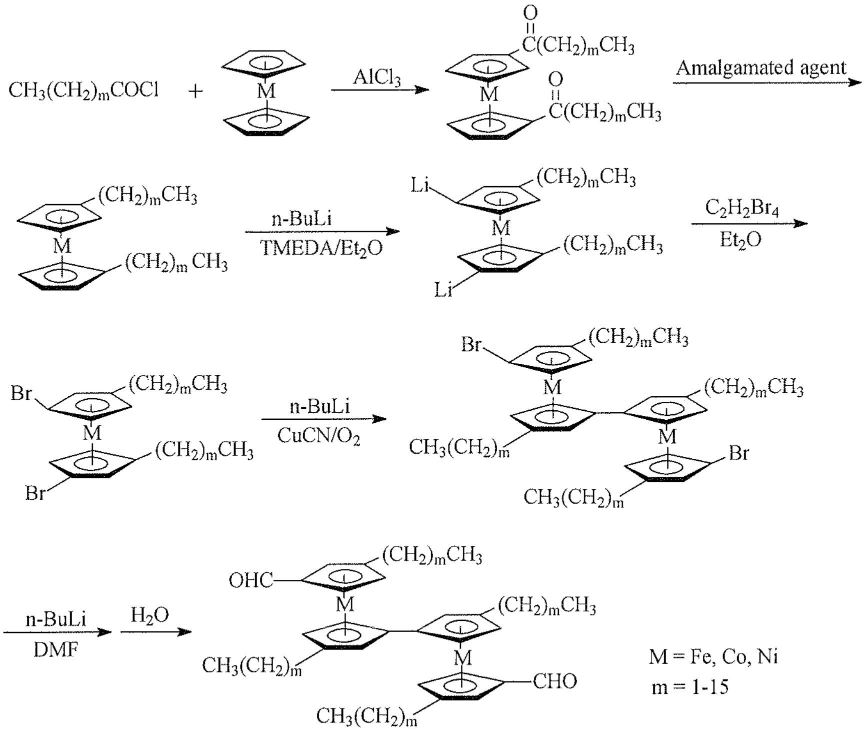
Further, monomer **XIV** metallocene containing bis(1-chloro-2,2-dicyanovinyl) with long flexible side chains was also synthesized:



XIV

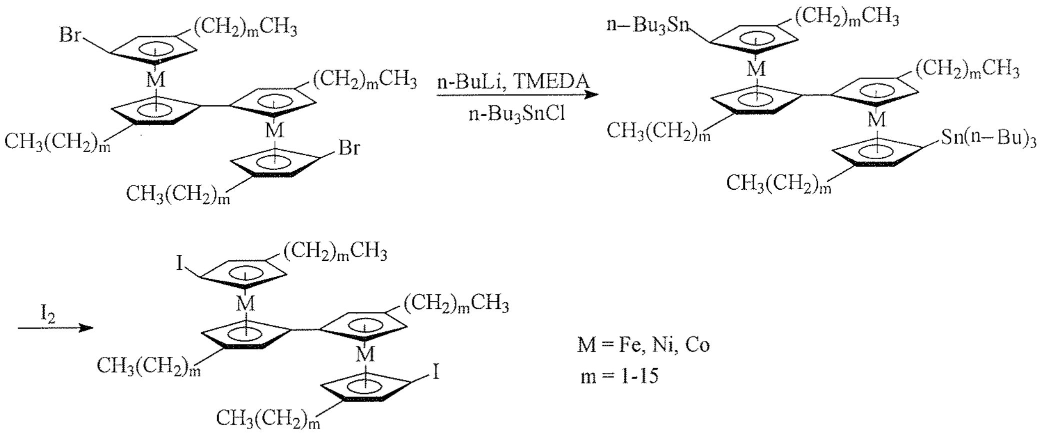
2. Synthesis of Bimetallocene-Containing Monomer with Long Flexible Side Chain

In another embodiment of the invention, bimetallocene monomers with dialdehyde were synthesized with long flexible side chains having the chemical structure **XV**:



XV

Bimetallocene monomers **XVI** with diiodo groups and long flexible side chains were synthesized following the reaction scheme:



XVI

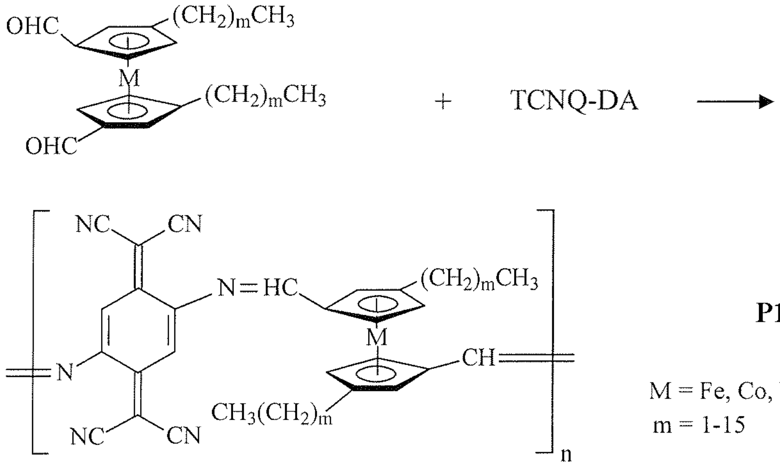
The rationale for the synthesis of bimetallocenes was based upon the fact that doubling the number of metallocene groups would enhance significantly the ferromagnetic behavior of the polymers to be synthesized, because of their easy formation of mixed-valence Fe(II)-Fe(III) species and charge transfer complex.

Polymerization of Electron-Acceptor Monomer with Metallocene-Containing Electron-Donor Monomer

The synthesis of molecule-based magnetic polymers with the formation of D^+A^- type CT complex or metal-radical complex was carried out by solution polymerization of an electron donor monomer (a modified metallocene- or bimetallocene-containing monomer with long flexible, hydrophobic side chains) with an electron-acceptor monomer **(I-IX)** containing tetracyano, bicyano, verdazyl, or thioaminyl radicals. The final step of polymerization is shown in the following schemes:

Polymerization of Metallocene-Containing Monomer with Long Flexible Side Chain and Monomer with Multiple Unpaired Electrons

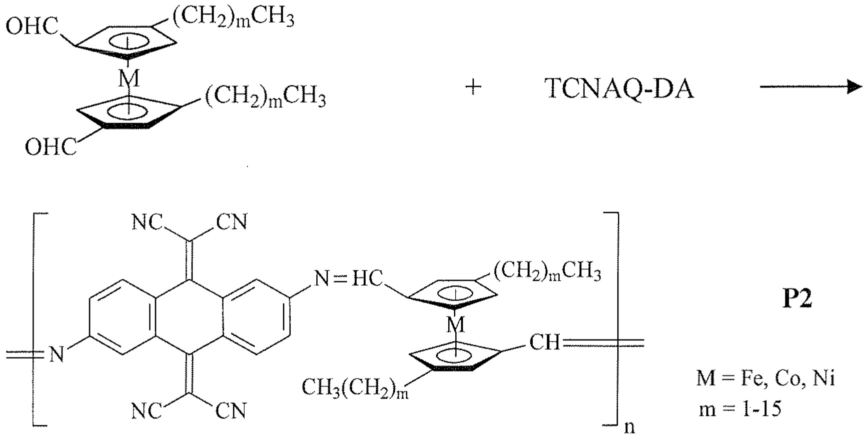
(1)



P1

M = Fe, Co, Ni
m = 1-15

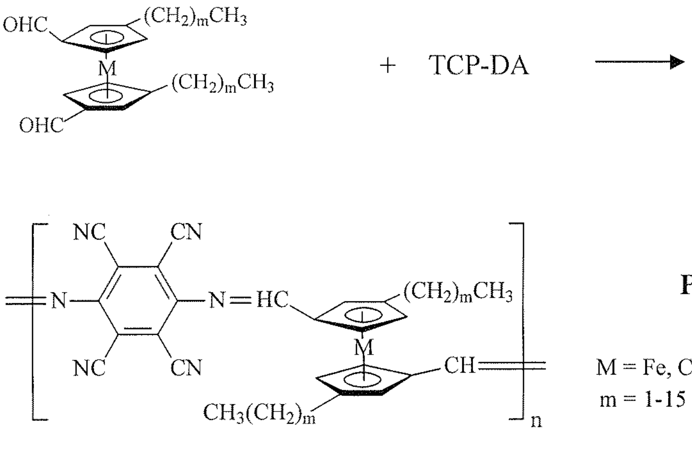
(2)



P2

M = Fe, Co, Ni
m = 1-15

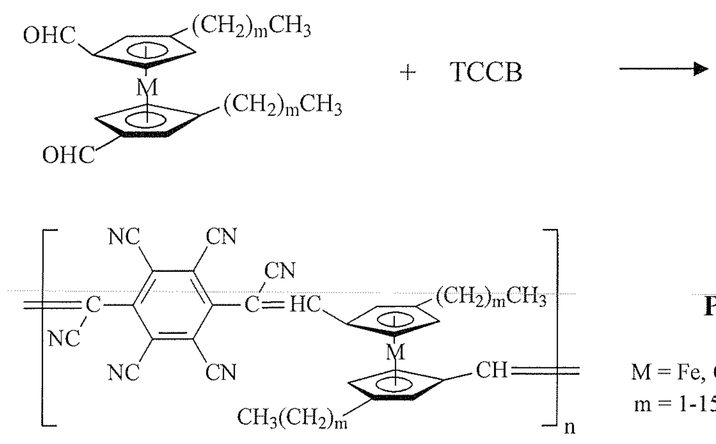
(3)



P3

M = Fe, Co, Ni
m = 1-15

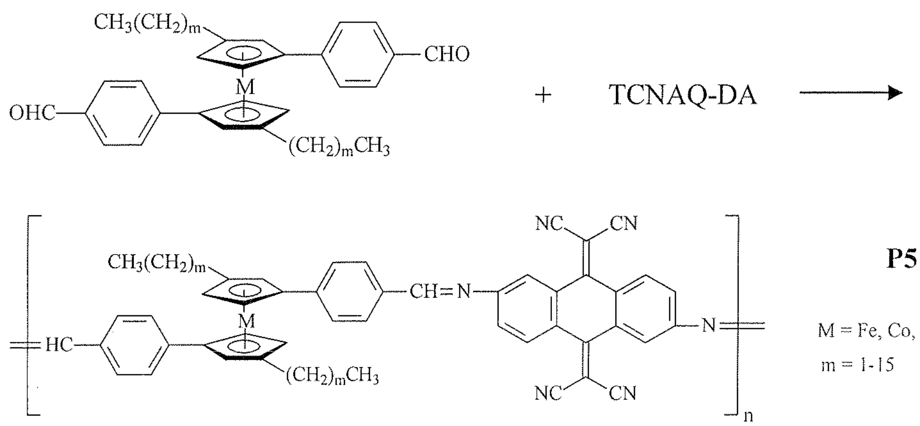
(4)



P4

M = Fe, Co, Ni
m = 1-15

(5)

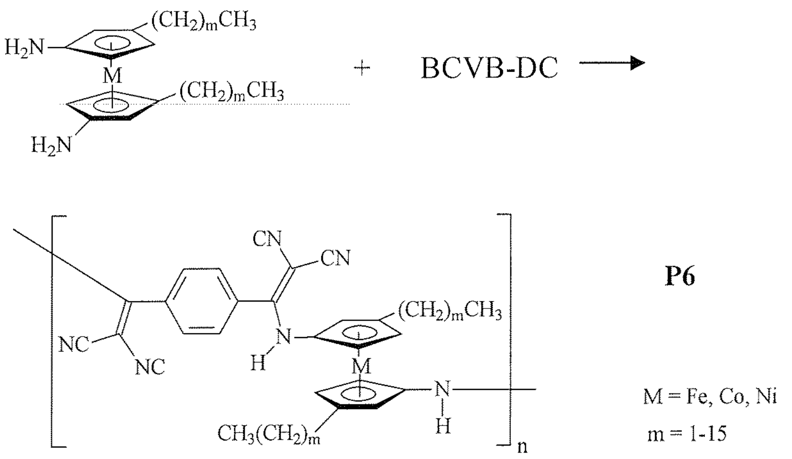


P5

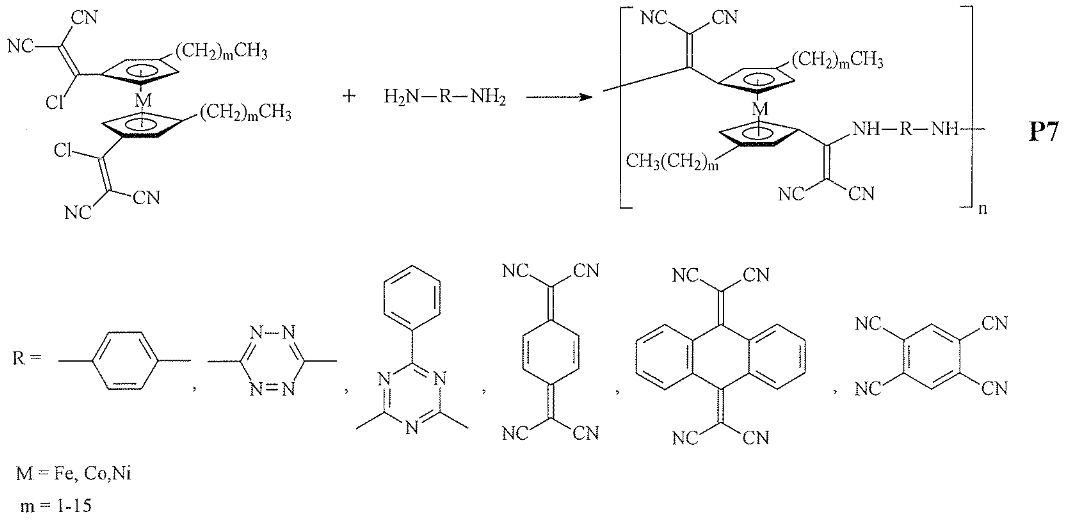
M = Fe, Co, Ni
m = 1-15

In the case of polymers **P1**, **P2**, **P3**, and **P4**, the strong electron donor of metallocene unit along the macromolecular chain delocalizes via -CH=N- bridge to the strong electron acceptor of the tetracyano unit, leading to the strong intramolecular exchange interactions, whereas the intermolecular superexchange coupling will occur due to the polarization of both metallocene and tetracyano units. Also, the entanglement of macromolecular chains will facilitate the expanding of the one-dimensional spin coupling into a three-dimensional one. This unique feature of a one-to-one covalently bonded connection between the electron donor and acceptor units can readily be distinguished from a small-molecule CT complex, the magnetic properties of which largely depend on the perfection of crystals or aggregates (any disruption of crystals or change of configuration will affect the three-dimensional spin coupling and thus low T_c). **P5** has higher molecular weight than **P1-P4**, due to the higher reactivity of aldehyde group in monomer **XI**. Unfortunately, the incorporation of phenyl group in monomer **XI** also leads to relatively lower magnetic properties because the enlarged distance between tetracyano- and ferrocene-units.

(6)



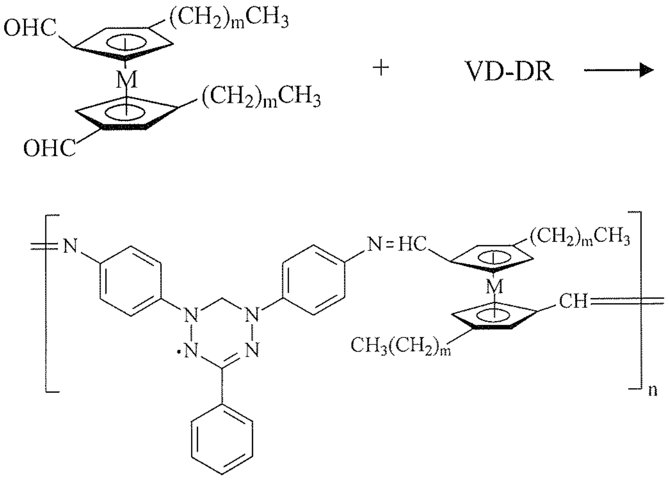
(7)



Poly(enaminonitriles) **P6** and **P7** were synthesized by interfacial polymerization. The –NH- group in the poly(enaminonitriles) can be doped to become a fully conjugated structure, and thus facilitate the magnetic interactions along the macromolecular chains.

Polymerization of Metallocene-Containing Monomer with Long Flexible Side Chain and Monomer with Stable Radicals

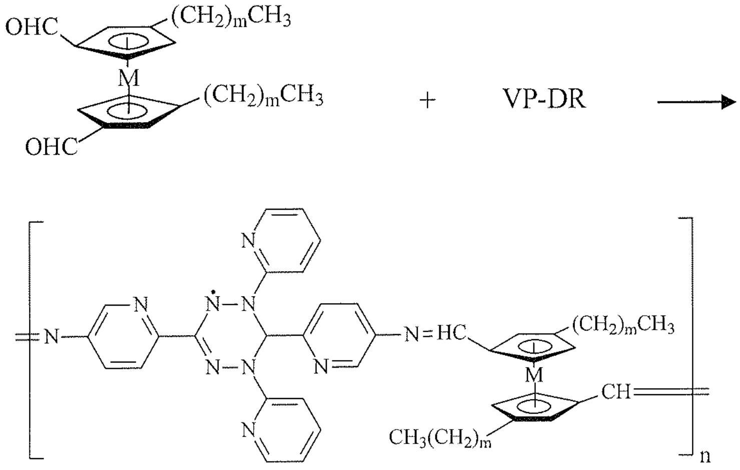
(8)



P8

M = Fe, Co, Ni
m = 1-15

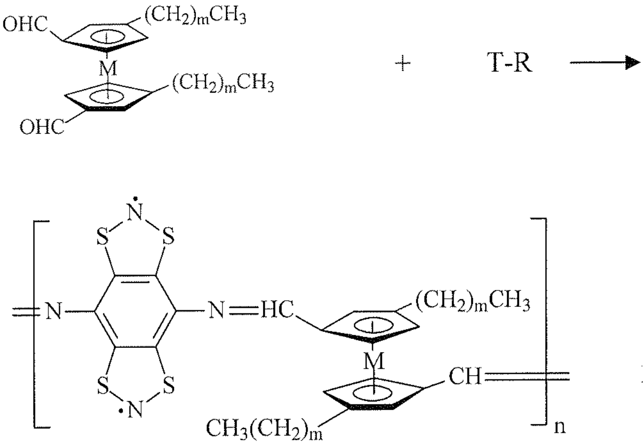
(9)



P9

M = Fe, Co, Ni
m = 1-15

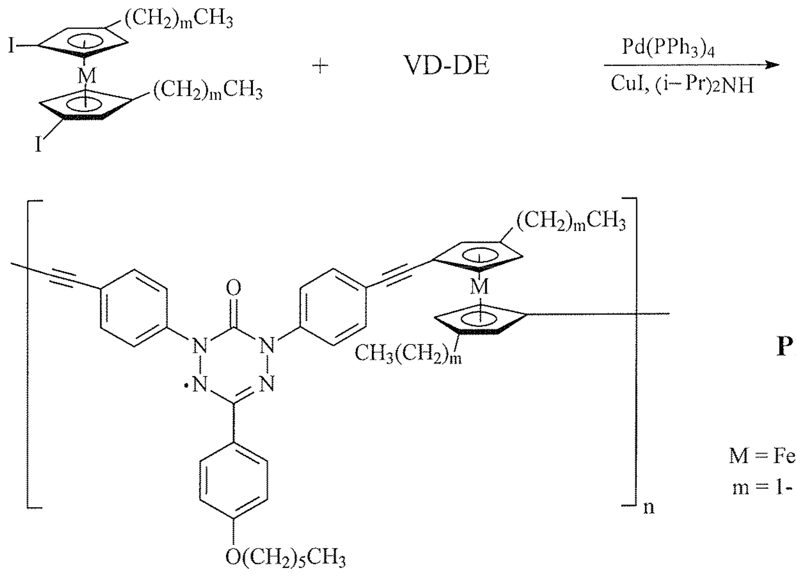
(10)



P10

M = Fe, Co, Ni
m = 1-15

(11)



P11

M = Fe, Co, Ni
m = 1-15

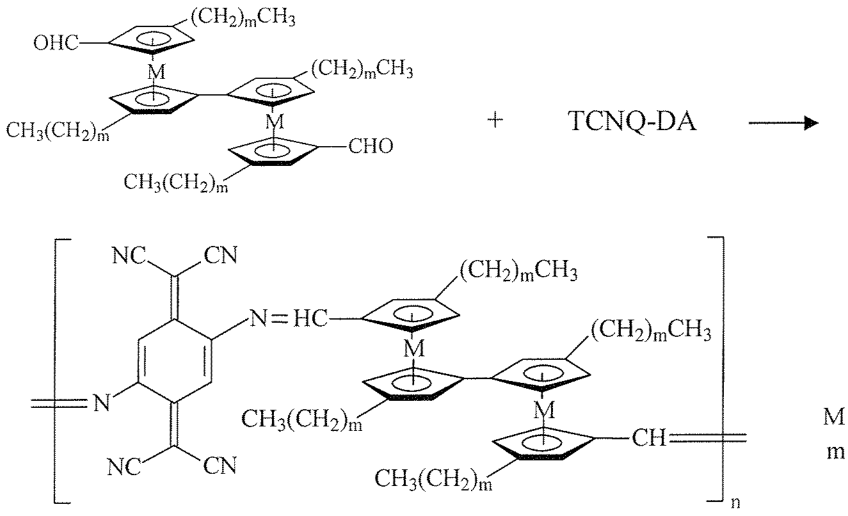
The stable radicals, i.e. verdazyl and thioaminyl radicals, are the premise for the success of polymers **P8**, **P9**, **P10**, and **P11**. The delocalization of electron spin of radical in the verdazyl or thioaminyl unit to the high-spin metallocene unit ensures the intramolecular spin coupling along the macromolecular chains of these polymers, while the strong intermolecular coordination capability between the verdazyl or thioaminyl unit and metallocene unit will generate a three-dimensional superexchange coupling. Also, the pyridyl group in polymer **P9** paves a way to introduce pyridinyl radicals or pyridinium complex, which will enhance the polarization of the verdazyl unit and subsequently increase the spin number or spin coupling in the polymer matrix. These polymers are regarded as being molecule-based giving rise to strong magnetic properties with high T_c.

Polymerization of Electron-Acceptor Monomer with Bimetallocene-Containing Electron-Donor Monomer

In further embodiments of the invention, further polymerizations were conducted with each of the nine monomers **I** (tetracyanoquinodiamine), **II** (tetracyanoanthraquinodiamine), **III** (tetracyano-*p*-phenylenediamine), **IV** (1,2,4,5-Tetracyano-3,6-bis-cyanomethyl-benzene), **VI** (verdazyl-type diamine radical), **VIII** (verdazyl-pyridyl-type diamine radical), **IX** (thioaminyl radical), or **VII** (verdazyl-type diethynyl radical) using a chemically modified biferrocene (dicarbaldehyde or diiodo) with long, hydrophobic flexible side chains. The synthesis routes are shown below.

Polymerization of Bimetallocene-Containing Monomer with Long Flexible Side Chain and Monomer with Multiple Unpaired Electrons

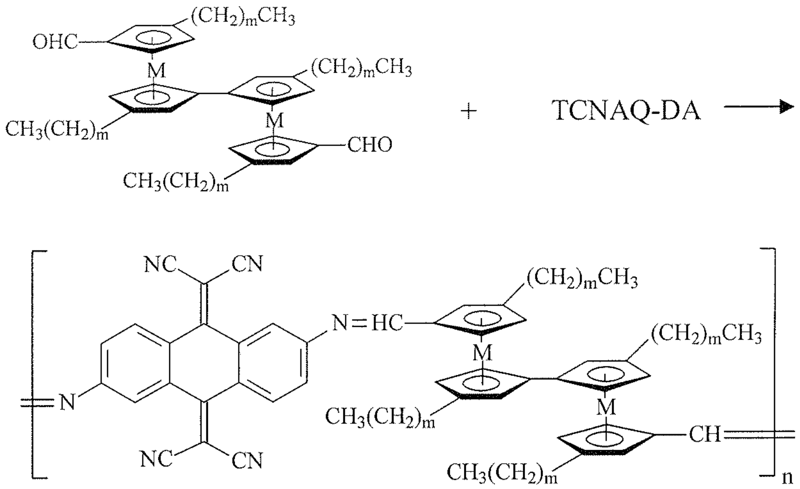
(12)



P12

M = Fe, Co, Ni
m = 1-15

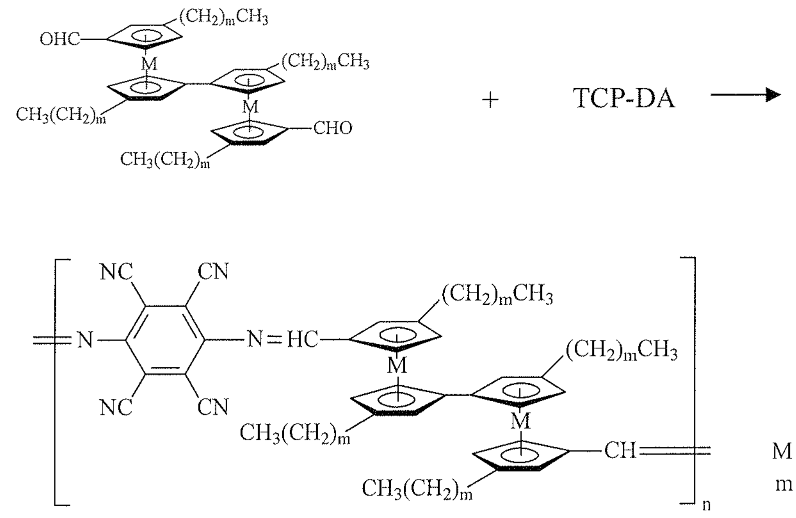
(13)



P13

M = Fe, Co, Ni
m = 1-15

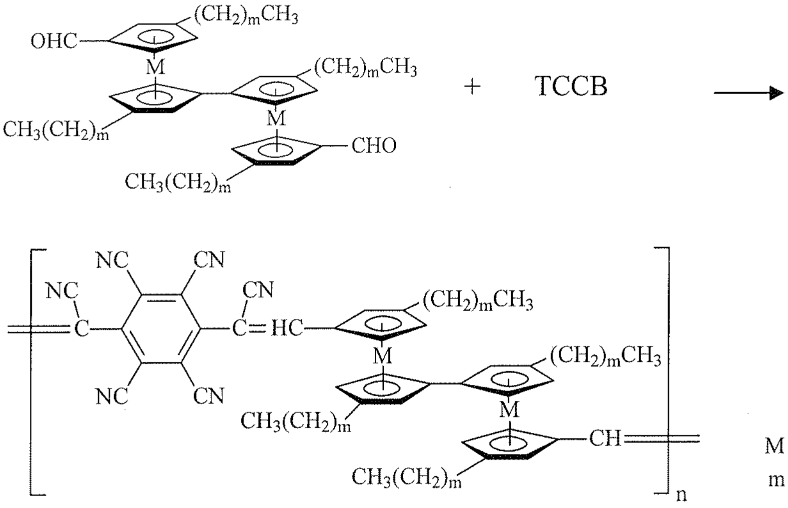
(14)



P14

M = Fe, Co, Ni
m = 1-15

(15)

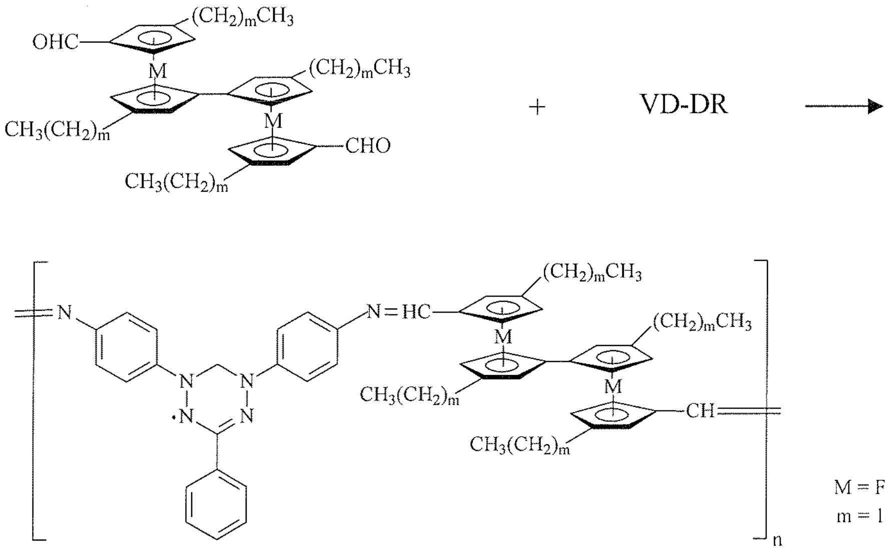


P15

M = Fe, Co, Ni
m = 1-15

Polymerization of Bimetallocene-Containing Monomer with Long Flexible Side Chain and Monomer with Stable Radicals

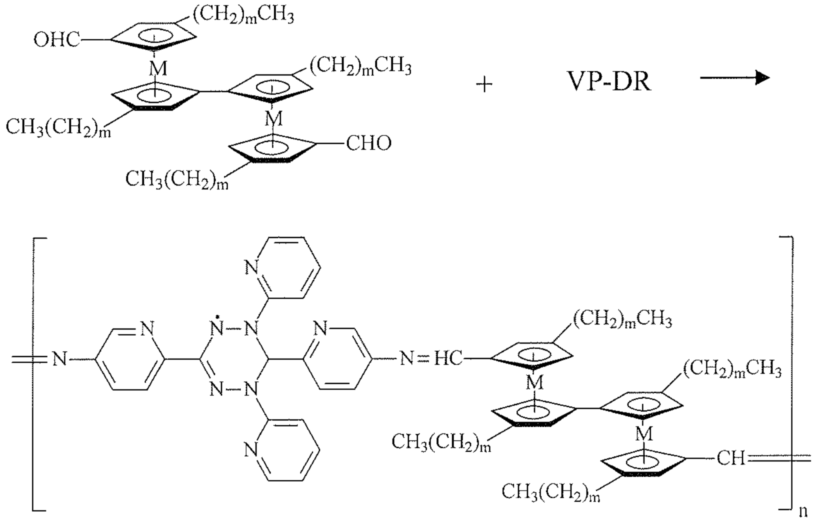
(16)



P16

M = Fe, Co, Ni
m = 1-15

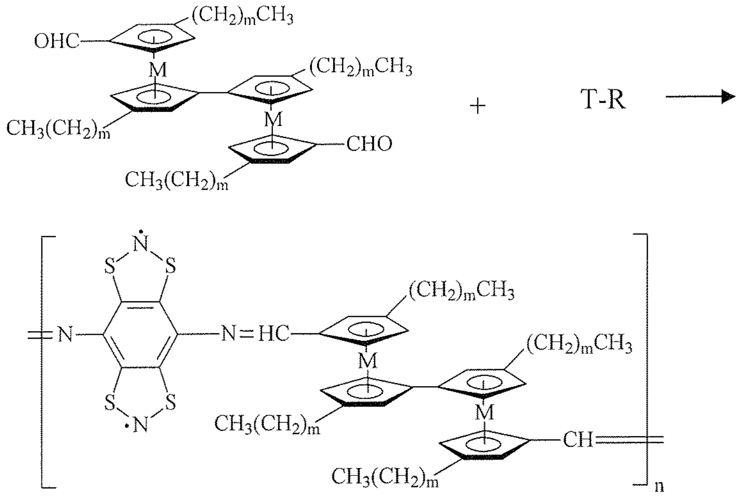
(17)



P17

M = Fe, Co, Ni
m = 1-15

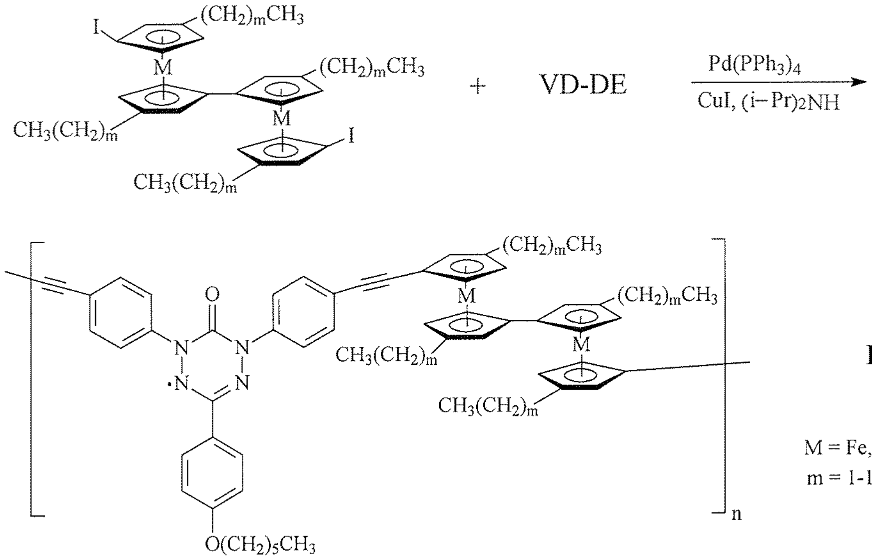
(18)



P18

M = Fe, Co, Ni
m = 1-15

(19)



P19

M = Fe, Co, Ni
m = 1-15

The synthesis procedures for a series of high-T_c molecule-based magnetic polymers is provided along with the presentation of representative properties of the synthesized magnetic polymers via X-ray diffraction (XRD) and electron spin resonance (ESR) spectrometry. As seen in FIG. 2a, XRD pattern (intensity versus two-theta angle) for the molecule-based magnetic polymer **P5** is shown. The XRD pattern for **P5** is clearly distinct from the XRD pattern for iron oxide as shown in FIG. 2b. In particular, the XRD pattern for **P5** has no reflection peaks for the values of 2θ ranging from 30 to 70 degrees, whereas iron oxide has several reflection peaks in the same range of 2θ values. Thus we can conclude that **P5** is substantially devoid of iron oxide. FIG. 3 shows an ESR spectrum of the molecule-based magnetic polymer **P5**. The ESR spectrum indicates the presence of spin-spin interactions between the constituent monomers that constitute the **P5** magnetic polymer.

As seen in FIGS. 2 and 3, the properties of the molecule-based magnetic polymer include: (1) they are substantially free of any magnetic metallic particles and thus are homogeneous (FIG. 2), (2) they exhibit the presence of spin-spin interactions between the constituent components within the polymer (FIG. 3). Further, the polymers synthesized are soluble in common solvents, as shown in FIGS. 4a – 4c, offering good processability. The synthesized polymer according to the invention is soluble as a 0.1 wt% in THF in FIG. 4a, 1.0 wt% in THF in FIG.4b and 10.0 wt% in THF in FIG. 4c.

In one embodiment of the invention, a magnetorheological fluid is prepared by mixing polymerized magnetic polymers **P1-P19**, either alone or in combination with each other, with a suitable carrier solvent. These magnetic polymer-based magnetorheological fluids can replace conventional magnetic fluids currently found in the marketplace.

Based upon the foregoing disclosure, it should now be apparent that the method of preparing molecule-based magnetic polymers and use of these polymers in preparing magnetic fluids described herein will carry out the objects set forth hereinabove. It is, therefore, to be understood that any variations evident fall within the scope of the claimed invention and thus, the selection of specific component elements can be determined without departing from the spirit of the invention herein disclosed and described.

Claims

What is claimed is:

1. A magnetic polymer comprising:

repeating units of an organometallic monomer covalently bonded to a monomer having a plurality of unpaired electrons.

2. The magnetic polymer of claim 1, wherein the organometallic monomer is a metallocene.

3. The magnetic polymer of claim 2, wherein the metallocene is a ferrocene-, cobaltocene-, nickelocene-modified, biferrocene-, bicobaltocene-, or binickelocene compound.

4. The magnetic polymer of claim 3, wherein the metallocene is modified with at least one aldehyde, iodo, or chloro group having alkyl side chains.

5. The magnetic polymer of claim 1, wherein the monomer having a plurality of unpaired electrons is tetracyanoquinodiamine, tetracyanoanthraquinodiamine, tetracyano-*p*-phenylenediamine, 1,2,4,5-Tetracyano-3,6-bis-cyanomethyl-benzene, or 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene.

6. A magnetic polymer comprising:

repeating units of an organometallic monomer covalently bonded to a stable free-radical based monomer.

7. The magnetic polymer of claim 6, wherein the organometallic monomer is an electron-donor metallocene.

8. The magnetic polymer of claim 7, wherein the metallocene is a ferrocene-, cobaltocene-, or nickelocene-, biferrocene-, bicobaltocene-, or binickelocene-modified compound.

9. The magnetic polymer of claim 8, wherein the metallocene is modified with at least one aldehyde, iodo, or chloro group having alkyl side chains.

10. The magnetic polymer of claim 6, wherein the stable free-radical based monomer is a verdazyl free radical, or a thioaminyl free radical.

11. The magnetic polymer of claim 10, wherein the verdazyl free radical is a verdazyl diamine free radical, or a verdazyl diethynyl free radical, and the thioaminyl free radical is a thioaminyl diamine free radical.

12. A method of preparing a magnetic polymer, the method comprising the steps of:
preparing an organometallic monomer;
preparing a monomer having a plurality of unpaired electrons; and
polymerizing the organometallic monomer and monomer having a plurality of unpaired electrons to form a magnetic polymer.

13. The method of claim 12, wherein the organometallic monomer is a bimetallocene.

14. The method of claim 13, wherein the metallocene is a biferrocene-, bicobaltocene-, or binickelocene-modified compound.

15. The method of claim 14, wherein the biferrocene-, bicobaltocene-, or binickelocene-modified compound is modified with at least one aldehyde group, iodo, or chloro having alkyl side chains.

16. A method of preparing a magnetic polymer, the method comprising the steps of:
preparing an organometallic monomer;
preparing a stable free-radical based monomer; and
polymerizing the organometallic monomer and the stable free-radical based monomer to form a magnetic polymer.

17. The method of claim 16, wherein the organometallic monomer is a bimetallocene.

18. The method of claim 17, wherein the metallocene is a biferrocene-, bicobaltocene-, or binickelocene-modified compound.

19. The method of claim 18, wherein the biferrocene-, bicobaltocene-, or binickelocene-modified compound is modified with at least one aldehyde group, iodo, or chloro having alkyl side chains.

20. The method of claim 16, wherein the free-radical based monomer is a verdazyl free radical or a thioaminyl free radical.

21. The method of claim 20, wherein the verdazyl free radical is a verdazyl diamine free radical, or a verdazyl diethylnyl free radical, and the thioaminyl free radical is a thioaminyl diamine free radical.

22. A magnetorheological fluid comprising:

a carrier solvent; and

a magnetic polymer soluble in the carrier solvent, wherein the magnetic polymer comprises repeating units of an organometallic monomer covalently bonded to a monomer having a plurality of unpaired electrons.

23. The magnetorheological fluid of claim 22, wherein the organometallic monomer is a metallocene.

24. The magnetorheological fluid of claim 23, wherein the metallocene is a ferrocene-, cobaltocene-, nickelocene, biferrocene-, bicobaltocene-, or binickelocene-modified compound.

25. The magnetorheological fluid of claim 23, wherein the metallocene is modified with at least one aldehyde, iodo, or chloro group having alkyl side chains.

26. The magnetorheological fluid of claim 23, wherein the monomer having a plurality of unpaired electrons is tetracyanoquinodiamine, tetracyanoanthraquinodiamine, tetracyano-*p*-phenylenediamine, 1,2,4,5-Tetracyano-3,6-bis-cyanomethyl-benzene, or 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene.

27. The magnetorheological fluid of claim 22, wherein the carrier solvent is an organic solvent.

28. The magnetorheological fluid of claim 22, wherein the carrier solvent is an aqueous solvent.

29. A magnetorheological fluid comprising:

a carrier solvent; and

a magnetic polymer soluble in the carrier solvent, wherein the magnetic polymer comprises repeating units of an electron-donor metallocene-containing monomer covalently bonded to a stable free-radical based monomer.

30. The magnetorheological fluid of claim 29, wherein the metallocene is a ferrocene-, cobaltocene-, nickelocene-, biferrocene-, bicobaltocene-, or binickelocene-modified compound.

31. The magnetorheological fluid of claim 30, wherein the metallocene is modified with at least one aldehyde, iodo, or chloro group having alkyl side chains.

32. The magnetorheological fluid of claim 29, wherein free-radical based monomer is a verdazyl free radical or a thioaminyl free radical.

33. The magnetorheological fluid of claim 29, wherein the verdazyl free radical is a verdazyl diamine free radical or a verdazyl diethylnyl free radical, and the thioaminyl free radical is a thioaminyl diamine free radical.

34. The magnetorheological fluid of claim 33, wherein the carrier solvent is an organic solvent.

35. The magnetorheological fluid of claim 29, wherein the carrier solvent is an aqueous solvent.

36. A method of preparing a magnetorheological fluid, the method comprising the steps of:
preparing a magnetic polymer comprising the steps of:
preparing an electron-donor metallocene-containing monomer;
preparing a monomer having a plurality of unpaired electrons; and
polymerizing the electron-donor metallocene-containing monomer and monomer having a plurality of unpaired electrons to form the magnetic polymer; and
mixing the magnetic polymer with a carrier solvent.

37. The method of claim 36, wherein the electron-donor organometallic monomer is a metallocene.

38. The method of claim 37, wherein the metallocene is wherein the metallocene is a ferrocene-, cobaltocene-, nickelocene-, biferrocene-, bicobaltocene-, or binickelocene-modified compound.

39. The method of claim 38, wherein the metallocene is modified with at least one aldhehyde group, iodo, or chloro having alkyl side chains.

40. The method of claim 36, wherein the carrier solvent is an organic solvent.

41. The method of claim 36, wherein the carrier solvent is an aqueous solvent.

42. A method of preparing a magnetorheological fluid, the method comprising the steps of:
preparing a magnetic polymer comprising the steps of:
preparing an electron-donor metallocene-containing monomer;

preparing a preparing a stable free-radical based monomer; and

polymerizing the electron-donor metallocene-containing monomer and the stable free-radical based monomer to form the magnetic polymer; and

mixing the magnetic polymer with a carrier solvent.

43. The method of claim 42, wherein the electron-donor organometallic monomer is a metallocene.

44. The method of claim 43, wherein the metallocene is a ferrocene-, cobaltocene-, nickelocene-, biferrocene-, bicobaltocene-, or binickelocene-modified compound.

45. The method of claim 44, wherein the metallocene is modified with at least one aldhehyde group, iodo, or chloro having alkyl side chains.

46. The method of claim 42, wherein free-radical based monomer is a verdazyl free radical or a thioaminyl free radical.

47. The method of claim 46, wherein the verdazyl free radical is a verdazyl diamine free radical or a verdazyl diethylnyl free radical, and the thioaminyl free radical is a thioaminyl diamine free radical.

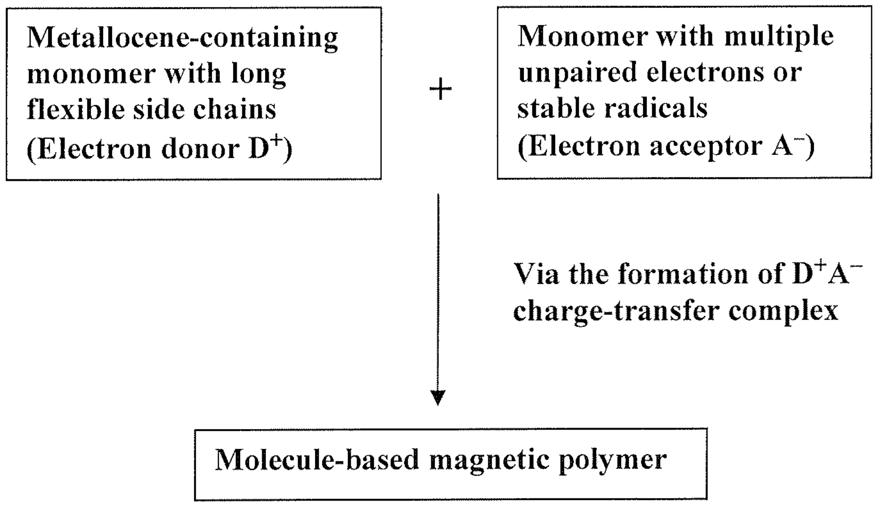
48. The method of claim 47, wherein the verdazyl free radical is a verdazyl-pyridyl diamine free radical.

49. The method of claim 42, wherein the carrier solvent is an organic solvent.

50. The method of claim 42, wherein the carrier solvent is an aqueous solvent.

Synthesis Routes for the Proposed Molecule-Based Magnetic Polymers

(I) Metallocene-Containing Molecule-Based Magnetic Polymer



(II) Bimetallocene-Containing Molecule-Based Magnetic Polymer

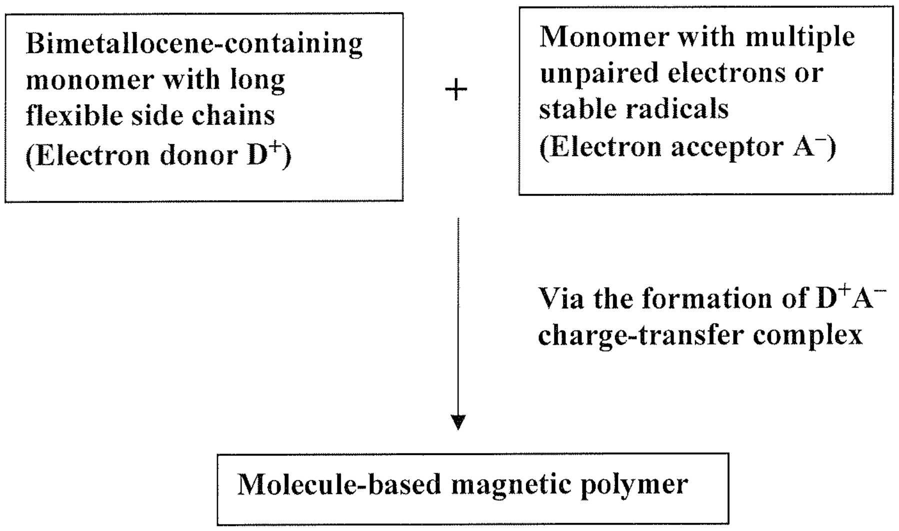


FIG. 1

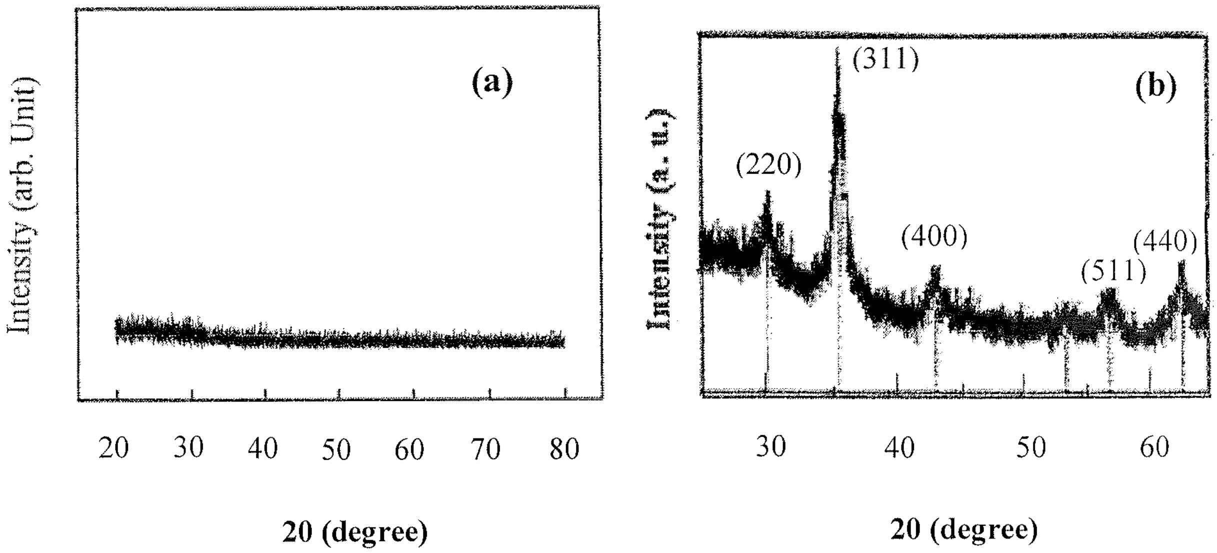

(a)
Intensity (arb. Unit)
20
30
40
50
60
70
80
2θ (degree)
(b)
Intensity (a. u.)
(311)
(220)
(400)
(511)
(440)
30
40
50
60
2θ (degree)

Fig. 2

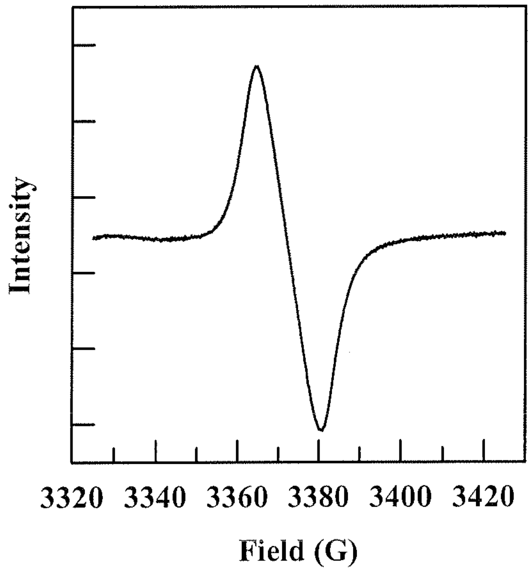
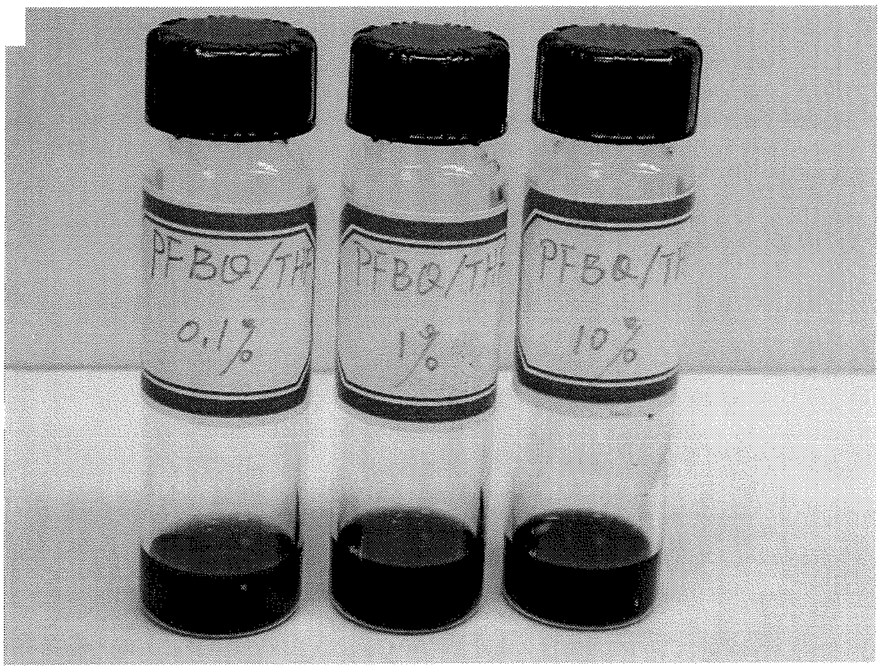


FIG. 3



(a) 0.1 wt% in THF **(b) 1 wt% in THF** **(c) 10 wt% in THF**

FIG. 4