(54) Title: SELF-ASSEMBLING COMPOUNDS AND USE OF THE SAME TO INDUCE ORDER IN ORGANIC MEDIA

(57) Abstract: Self-assembling compounds capable of forming birefringent gels when added to an organic medium in an amount of about 0.05 % to about 2 % by weight are disclosed. A birefringent gel containing a self-assembling compound and an organic monomer can be polymerized to produce an optically birefringent polymer. The birefringent polymer can be melted to provide a birefringent melt that then can be formed into an article of manufacture, like an optical fiber.
SELF-ASSEMBLING COMPOUNDS AND USE OF THE SAME TO INDUCE ORDER IN ORGANIC MEDIA

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. provisional patent application Serial No. 60/155,178, filed September 21, 1999.

FIELD OF THE INVENTION

The present invention relates to self-assembling compounds capable of forming a birefringent gel when added to an organic medium, such as an organic solvent or an organic monomer, in an amount of about 0.05% to about 2% by weight, based on the weight of the organic medium. A birefringent gel comprising the self-assembling compound and an organic monomer can be polymerized to form a birefringent polymer. The present invention also relates to a method of manufacturing an article from the birefringent gel or a birefringent melt of the birefringent polymer. A self-assembling compound is a block oligomer or polymer, containing a flexible block, a rigid block, and a dendritic block, wherein the bonds between the blocks are covalent bonds.

BACKGROUND OF THE INVENTION

Research directed to finding materials having unexpected properties or functionality based on the self-ordering or folding of molecules is intense. Recent research in this area has made

A less investigated research area is self-assembling structures that change the structure of macromolecules, e.g., act as "scaffolds," and, therefore, have the ability to profoundly change the properties of polymers. It has been theorized that molecular "scaffolds," analogous to chaperones that exist in nature to promote proper folding of proteins (T. Langer et al., *Nature*, 356, 683 (1992); J. Frydman et al., *Nature*, 370, 111 (1994); M.J. Todd et al., *Science*, 265, 659 (1994)), likewise can transform the bulk of a material into a new useful structure.
In particular, over the last decade research groups have attempted to prepare materials having an improved structure. These materials often are polymer composites, such as a composite containing a polystyrene component and a liquid crystal (LC) polymer component. However, most of these attempts failed because the components of the composite are immiscible, which leads to microphase separation. Typically, in order to render such composites physically compatible, a chemical modification of the polystyrene component (e.g., sulfonation) is required.

On the other hand, amorphous polystyrene can be oriented by applying an external mechanical field. For example, melt-drawn polystyrene fibers exhibit weak birefringence on the order of -0.02. However, such flow-induced birefringence is not a permanent property of the polymer, and birefringence completely disappears when the melt-drawn polystyrene fibers are heated above their glass transition temperature ($T_g$).

Birefringence is a property that is well known to persons skilled in the art of ordered materials, such as liquid crystals, and its measurement is a standard methodology used to determine whether a material exhibits long-range orientational or positional order. As illustrated hereafter, a material that exhibits birefringence is ordered, i.e., has a long-range molecular orientation or has domains of oriented molecules. Birefringence of a material is demonstrated using a bipolar microscope, wherein an ordered material rotates incident light from the microscope, and the light is transmitted
through the material. Materials that lack order, i.e., are amorphous or glassy, scatter the incident light and appear dark when viewed through a bipolar microscope. In some systems, the observed transmitted light can be attributed, partially or completely, to the highly ordered, self-assembled DRC structure in the gels or polymers.

Attempts to modify an amorphous polymer, and thereby impart order to the polymer, are directed to improving a property of the polymer or overcoming a disadvantage associated with the polymer. For example, one of the biggest disadvantages associated with atactic, amorphous polystyrene is brittleness. In order to overcome this problem, polymers have been subjected to either uniaxial or biaxial orientation, which results in a brittle to ductile transition due to induced anisotropy. Therefore, when a clear product is desired, oriented polymeric sheets (OPS) are used.

The present invention is directed to self-assembling compounds, or molecules, that have the ability to form nanostructures, orient, or change the structure of organic media, including the coiled macromolecules of a typical amorphous, glassy polymer. The present compounds are linear, and form scaffold-like aggregates of a nanoscale dimension, in the form of ribbon, which impart order to otherwise disordered organic media, and improve the properties of the organic media.
SUMMARY OF THE INVENTION

The present invention is directed to self-assembling compounds that improve the properties of polymeric materials, such as polystyrene, poly-(methyl methacrylate), and other acrylic polymers, which are commercial polymers having numerous applications. In particular, modification of an organic medium, such as polystyrene or an organic solvent, can be achieved using a compound of the present invention, termed a dendron-rodcoil or DRC compound, as an additive in small quantities to impart liquid crystal-like (LC) properties to organic media, like a polymer, and thereby impart improved optical, mechanical, and/or thermal properties to conventional amorphous and semi-crystalline polymers that otherwise have been unattainable.

Because a very small amount of a present DRC compound is needed to induce LC-like properties in organic media, the resulting ordered polymer is economically feasible, and costs considerably less than commercially available LC polymers. Thus, one aspect of the present invention is to provide a new and simple method of producing low-cost polymers having the highly advanced physical properties of expensive liquid crystalline polymers. In one embodiment, this aspect is achieved by imparting order to amorphous, glassy polymers using a present DRC compound. It also is possible to change the properties of polymers that are semi-crystalline in nature, i.e., are not completely amorphous.

In particular, long-range order and the accompanying improved properties are imparted to an
amorphous or semi-crystalline polymer by the addition of about 0.05% to about 2%, by weight of the polymer, of a present DRC compound to the polymer. A DRC compound of the present invention is a crystalline material that is miscible with organic solvents and monomers. After monomer polymerization, the resulting polymer composite behaves like a homogeneous LC phase in that the polymer remains birefringent, i.e., is molecularly oriented, over a broad temperature range of up to 300°C (e.g., 200°C above the glass transition temperature of polystyrene). This property allows a substantially greater orientation of the polymer during a melt-drawing process, including the manufacture of fibers, compared to that presently achieved using pure glassy polymers, such as polystyrene.

Therefore, one aspect of the present invention is to provide a compound having the ability to orient organic media, such as organic solvents and organic monomers.

Another aspect of the present invention is to provide a compound having the ability to orient the macromolecular chains of an amorphous or semi-crystalline polymer and impart order, and, accordingly, improved properties, to the polymer.

A compound of the present invention is a dendron-rodcoil, or DRC, which is a block oligomer or polymer having a branched block (dendron), a rigid block (rod), and a flexible block (coil), wherein the bonds between the blocks are covalent bonds.

A dendron-rodcoil, or DRC, compound can be depicted by the following three general structures:
wherein D is the dendritic block, R is the rod block, and C is the coil block, and wherein the bonds between the D, R, and C blocks are covalent bonds. The structure of the D, R, and C blocks, and the structure of the entire DRC molecule, is discussed in detail hereafter.

Another aspect of the present invention is the formation of a birefringent gel, or a gel capable of rotating light, of an organic medium prepared by adding about 0.05% to about 2%, by weight, of a DRC compound to the organic medium, for example, an organic solvent or an organic monomer. An organic monomer is defined herein as a gaseous or liquid organic compound having a functional group capable of undergoing a polymerization reaction. The functional group typically is a carbon-carbon double or triple bond, but also can be an epoxy group, for example. An organic solvent is a liquid organic compound that lacks a functional group capable of undergoing a polymerization reaction.

Another aspect of the present invention is the preparation of a birefringent polymer formed by polymerizing a birefringent gel comprising an organic monomer and a DRC material. The birefringent gel can further comprise metal ions to mineralize the birefringent polymer by forming inorganic materials templated by the DRC assemblies. The birefringent gel also can contain a crosslinker, a polymerization initiator, and other optional ingredients to achieve specific properties in the final product.
Yet another aspect of the present invention is to provide a method of manufacturing an article from a birefringent gel or a polymer prepared from a birefringent gel, comprising an organic monomer and a DRC compound. One method comprises melting the birefringent polymer to form a birefringent polymer melt, then forming the birefringent melt into the article, for example, drawing a fiber from the birefringent polymer melt to provide an optical fiber or molding the birefringent melt to form the article. Alternatively, an article can be formed by polymerizing the birefringent gel into a predetermined shape.

Still another aspect of the present invention is to provide a method of imparting order to an amorphous or semi-crystalline polymer by incorporating about 0.05% to about 2%, by weight of the polymer, of a DRC compound into the polymer.

Another aspect of the present invention is to provide a mineralized, ordered polymer by introducing metal ions into a polymer containing about 0.05% to about 2%, by weight, of a DRC compound.

Another aspect of the present invention is to admix the DRC compound with a gaseous monomer, like ethylene, then polymerize the resulting mixture to provide a polymer, or article prepared therefrom, having improved properties.

These and other novel aspects of the present invention will become apparent from the following detailed description of the preferred embodiments taken in conjunction with the figures.
BRIEF DESCRIPTION OF THE FIGURES

Fig. 1(A) contains photographs of birefringent dichloromethane gels containing a DRC compound of the present invention;

Figs. 1(B) and 1(C) contain photographs of polystyrene and poly(2-ethylhexyl methacrylate) containing a DRC compound and polystyrene and poly(2-ethylhexyl methacrylate) free of a DRC compound;

Fig. 2 contains a molecular representation of a linear DRC compound of structural formula (1), and NMR spectra of the DRC compound in THF (a solution) and dichloromethane (a gel);

Fig. 3 contains photographs of a small angle X-ray pattern of gel-derived polystyrene (A) and optical micrographs of the polystyrene taken between crossed polarizers showing birefringence at 100°C (B) and 250°C (C);

Fig. 4 contains photographs of polystyrene containing 1%, by weight, DRC compound (1) (left) and 1%, by weight, of a diblock RC compound (right), and molecular representations of the DRC compound and RC compound, and aggregates of each;

Fig. 5 contains X-ray diffraction patterns and optical micrographs of a pure polystyrene fiber (A, C, and E) and a polystyrene fiber containing 1%, by weight, DRC compound (1) (B, D, and F);

Fig. 6 is a transmission electron micrograph of osmium tetroxide treated polystyrene containing 1%, by weight, DRC compound (1);

Fig. 7 is a molecular representation of the bimolecular ribbon formed via self-assembly of linear DRC molecules of structural formula (1); and
Fig. 8 contains plots of Herman's orientation factor ($f$) vs. draw (or deformation) ratios ($\lambda$) for polystyrene (lower line) and polystyrene containing 1% by weight DRC compound (1) (higher line).

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The present invention is directed to self-assembling compounds that form a birefringent gel when added to an organic medium in an amount of about 0.05% to about 2%, by weight of the organic medium. If the organic medium is an organic monomer, the birefringent gel can be polymerized to form a birefringent polymer.

The present invention, therefore, is directed to improving the properties of polymers, like amorphous and semi-crystalline polymers, by inducing order in the polymers through incorporation of a small amount of a novel DRC compound into the polymer. The DRC compounds impart order to organic media, and convert amorphous and semi-crystalline polymers into composites that behave like liquid crystalline polymers, and, consequently, exhibit improved physical properties. The resulting composites exhibit little or no microphase separation, and, surprisingly, retain birefringence in the melt form and behave in the melt form like a liquid crystalline material. In particular, modification of amorphous polystyrene using a present dendron-rodcoil compound as additive, in small quantities, is specifically illustrated.
The advantages achieved and the problems solved by the present invention include, for example:

a) a very small amount of a DRC compound modifies a polymer and induces liquid crystalline-like (LC) order in the polymer;

b) the DRC compound and the polymer components of the composite are sufficiently compatible to prevent the composite from undergoing appreciable microphase separation. The absence of microphase separation provides improved optical properties relative to prior, immiscible blends of polystyrene and LC polymers;

c) the birefringent composite also can be oriented on a macroscopic level, thereby improving tensile strength and other mechanical properties compared to amorphous polystyrene; and

d) the composite remains highly birefringent, even at temperatures well above the T_g, even when no external mechanical field is applied, because the birefringence of the composite is attributed to intrinsic order in the material.

As previously stated, the present invention is directed to novel dendron-rodcoil (DRC) compounds that impart order to organic media at low concentrations of about 0.05% to about 2%, by weight of the media, and to polymers and articles of manufacture prepared from such ordered organic media. The novel DRC compounds are triblock oligomers or relatively low molecular weight polymers having a dendritic block (D), a rod block (R), and a coil block (C), wherein bonds between the various blocks are covalent bonds. In accordance with the present invention, the dendritic block has a branched struc-
ture. The rod block is rigid and unbranched, whereas the coil block is flexible and unbranched.

A DRC compound of the present invention has a general structural formula:

D-R-C, D-C-R, or C-D-R,

wherein D is the dendritic block, R is the rod block, and C is the coil block, and wherein the bonds joining the D, R, and C blocks are covalent bonds. Preferred embodiments of the present invention have the structure D-R-C.

As illustrated hereafter, the DRC compounds have a tendency to aggregate, which is attributed to the rigid, rod block and flexible, coil block of the compound. The DRC compounds also resist packing in three dimensions because the branched structure of the dendritic block prevents stacking of DRC molecules. The DRC compounds, therefore, associate to form a ribbon-like aggregate, as illustrated in Figs. 4 and 7, discussed hereafter. This ribbon-like aggregate of DRC molecules acts as a scaffold to impart order to organic media, such as organic solvents and organic monomers.

The coil block, C, is linear and flexible, and is an oligomer or polymer comprising one or more low molecular weight monomers. Block C has a weight average molecular weight (\( \bar{M}_w \)) of about 200 to about 10,000, and preferably about 200 to about 5,000. To achieve the full advantage of the present invention, block C has an \( M_w \) of about 200 to about 2,000. The beneficial properties of the C block, for example,
helping provide a capability for the DRC compounds to aggregate, have a tendency to decrease as the $M_w$ of the C block increases. However, this decrease in beneficial properties is overcome by simultaneously increasing the $M_w$ of the R block. This $M_w$ effect of the C and R blocks is discussed in more detail hereafter.

As stated above, a function of the C block is to promote aggregation of DRC molecules. The C block is linear and unbranched, which allows the C blocks of DRC molecules to come in close proximity to one another (see Fig. 4). The C block, therefore, comprises monomers that preferably are unsubstituted, or substituted with small moieties, which allows individual DRC molecules to come in close proximity to form a molecular ribbon of DRC molecules, as illustrated in Fig. 7. Large substituent moieties on the monomers comprising the C block, which hinder aggregation of DRC molecules, typically are avoided. The branched D blocks prevent intimate contact and entanglement of the C blocks of neighboring DRC molecules (see Fig. 4).

The monomers comprising the C block, therefore, can be any low molecular weight monomer that provides a flexible oligomer or polymer. If a hydrophobic C block is desired, the monomer can be ethylene, propylene, vinyl methyl ether, or a chlorinated or fluorinated vinyl monomer, e.g., vinyl chloride or vinylidene fluoride, for example. A hydrophilic C block can be prepared from a monomer like ethylene oxide or aziridine, for example.

The C block also can contain reactive groups for availability in a subsequent reaction,
for example, for entering into a polymerization reaction with an organic monomer after formation of a birefringent gel. Such a reactive C block is prepared from monomers like isoprene and butadiene, which provide a C block having carbon-carbon unsaturation. Reactive groups also can be present in the C block as pendant substituents on the backbone of the C block. For example, the C block can have hydroxy, amino, carboxy, or cyano groups as pendant substituents. The C block also can have other small, nonreactive, pendant substituents, like methyl, ethyl, isopropyl, isopropenyl, halo (especially F or Cl), and CF₃, for example.

The rod block, R, is linear and rigid, and is an oligomer or polymer of a monomer that provides a rigid polymeric structure. Block R has an Mₘ of about 200 to about 10,000, and preferably about 200 to about 5,000. To achieve the full advantage of the present invention, block R has an Mₘ of about 200 to about 2,000.

A function of the R block, like the C block, is to promote aggregation of DRC molecules to form a molecular ribbon of DRC molecules, as illustrated in Fig. 7. Aggregation and ribbon formation is adversely affected if the Mₘ of C block is too large. However, this adverse affect can be overcome by increasing the length, i.e., Mₘ, of the R block. It has been found that a ratio of C block monomer units to R block monomer units of about 2:1 to about 4:1, and preferably about 2.5:1 to about 3.5:1, provides preferred DRC compounds with respect to aggregation, forming a molecular ribbon, and imparting order to organic media.
The R block comprises one or more monomers that provide a rigid polymer. One such monomer, for example, is acetylene, which provides a rigid polymer having the general structure:

\[ \text{\textsuperscript{+}C-\textsuperscript{=}C-C=\textsuperscript{=}C=C=\textsuperscript{+}}. \]

The carbon-carbon double bonds of polyacetylene impart rigidity to block R, and provide reactive sites on the R block.

Other monomers useful in providing the rigid R block are bifunctional phenyl monomers, biphenyl monomers having a functional group on each phenyl ring, and a compound having the structure

![Chemical Structure](image)

wherein A is \((\text{CH}_2)_n\), O, S, or NH, wherein n is 1 or 2, and the Y groups, independently, are groups capable of undergoing a condensation reaction. For example, the Y groups are independently selected from moieties such as \(-\text{CO}_2\text{H}, -\text{COCl}, -\text{CO}_2\text{R}\) (wherein R is C\(_1\)-C\(_4\) alkyl), \(-\text{OH}, -\text{SH}, -\text{CONH}_2, -\text{CONHR}, -\text{NH}_2, -\text{NHR}, -\text{OSiR}_3\), and similar condensable moieties well known to persons skilled in the art. Preferred Y groups are \(-\text{CO}_2\text{H}, -\text{OH}, \text{and} -\text{OSiR}_3\).

To promote aggregation of DRC molecules into a bimolecular ribbon, the R block is not branched. This feature allows the R blocks of the DRC molecules to come in close proximity to one
another (Fig. 4), which assists aggregation because of \( \pi-\pi \) interactions between R blocks on neighboring DRC molecules.

The dendritic block D is branched and is prepared by reacting functional groups on the R block and/or C block with a suitably functionalized compound to incorporate branches into the DRC compound. The branched D block prevents DRC compounds from stacking in three dimensions, but allows the DRC molecules to aggregate and form a ribbon. As illustrated in Figs. 4 and 7, the D blocks of the DRC molecules aggregate to form a bimolecular species. The bimolecular species then aggregate to form DRC ribbons, or scaffolds.

The compound used to incorporate branching into the DRC compound typically is a polyfunctional compound having a substituent capable of condensing with a substituent on the R or C blocks, and having additional substituents for further branching. A compound used to form the D block also can contain nonreactive substituents, like CF\(_3\). In preferred embodiments, the D block is more hydrophilic than the R block, which assists in aggregation of the DRC compounds, for example by facilitating \( \pi-\pi \) interactions between aromatic rings in the R blocks of individual DRC molecules, and by promoting association of DRC molecules to form the bimolecular species by interactions such as hydrogen bonding through the D blocks. Increased hydrophilicity typically is achieved by having hydroxy substituents present on the D block.
An example of a compound used to incorporate branching, i.e., a dendritic block, into a DRC compound is

\[ \text{\includegraphics{image.png}} \]

wherein the Y groups, as defined above, are selected independently.

The following synthetic scheme illustrates the preparation of a DRC compound of the present invention. In particular, synthesis of triblock DRC compound (1) illustrated in the following scheme begins with the preparation of an oligoisoprene block C by anionic polymerization. Functionalization of the flexible coil block C using ethylene oxide then is performed to provide a hydroxy-terminated oligoisoprene. Functionalized block C then is condensed with a carboxyl-substituted biphenyl compound to form an ester linkage under mild conditions (i.e., DIPC, diisopropylcarbodiimide; DPTS, 4-(N,N-dimethylamino)pyridinium-4-toluenesulfonic acid; THF, tetrahydrofuran; HCl, hydrochloric acid, HF, hydrofluoric acid; RT, room temperature). The biphenyl compound also contained a tert-butyldimethylsilyl protecting group, and deprotection then was performed at -78°C using tetrabutylammonium fluoride (TBAF). Repetition of the esterification and depro-
tection reactions yielded a diblock compound containing flexible oligoisoprene and rigid biphenyl segments, i.e., a diblock containing the C and R segments. The third D block of DRC compound (1) is dendritic, and is synthesized by reacting a protected form of an A₂B-type monomer, i.e., 3,5-di-hydroxybenzoic acid, with the diblock RC compound. Esterification and deprotection reactions illustrated hereafter provided the DRC compound of structural formula (1) containing dendritic (D), rod (R), and coil (C) segments, or blocks.

The synthetic scheme that provides DRC compound (1), and details of each reaction set, are as follows:
The flexible oligoisoprene C block of DRC compound (1) contains, on average, about 9 monomeric isoprene units, and is structurally diverse, primarily containing the 3,4 addition product of isoprene. The C block imparts solubility to DRC compound (1), thereby allowing a self-assembly process to occur in solution or in the melt. The geometry of the dendron block D, and the coil block C, facilitate formation of one-dimensional self-assembled structures, or scaffolds, i.e., ribbons of bimolecular species of DRC molecules. Specifically, the bulkiness of the dendritic block D relative to rod block R prevents the formation of three-dimensional assemblies, i.e., stacks of DRC ribbons. The essentially identical aromatic rod-dendron blocks of DRC compound (1) strongly drive aggregation through noncovalent π-π interactions. The four hydroxy groups located on the periphery of dendritic block D provide an additional driving force for self-assembly of DRC compound (1) molecules through the formation of hydrogen bonds between DRC molecules.

The following is a detailed description of the synthesis of the DRC compound of structural formula (1). In general, unless otherwise stated, all starting materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) and benzene were redistilled from Na′/benzophenone ketyl. 1,3-Diisopropylcarbodiimide (DIPC) was distilled prior to use. 4-(N,N-dimethylamino)pyridinium-4-toluenesulfonate (DPTS) was prepared accordingly to published procedures. Isoprene was redistilled under nitrogen and dried over calcium hydride before use. Magnesium sulfate
(MgSO₄) was used to dry all organic solutions during work-up procedures. The silica used for flash chromatography was Silica Gel 60 (230-400 mesh), available from EM Sciences.

³¹H NMR spectra were recorded in THF-δ₆ or DMSO-δ₆ solution on a Varian Unity 500 (500 MHz) or Varian Unity 400 (400 MHz) spectrometer, using the solvent proton signal as a standard. ¹³C NMR spectra were recorded at 125 MHz on a Varian Unity 500 spectrometer using THF-δ₆ or DMSO-δ₆ as the solvent, and the solvent carbon signal as internal standard. Chemical shifts are expressed in parts per million (ppm). The following abbreviations are used in the following description of the synthesis: Ar' refers to aromatic rings derived from biphenyl fragments, Ar" refers to aromatic rings derived from 3,5-dihydroxybenzoic acid. Mass spectrometry was performed by the Mass Spectroscopy Laboratory at the University of Illinois, Urbana-Champaign, IL. High resolution field desorption mass spectra were collected on a Micromass 70-VSE spectrometer operating at 8 KV acceleration voltage and 4 KV extraction plate voltage. Matrix assisted laser desorption ionization (MALDI) mass spectra were obtained on a VG TofSpec spectrometer using dithranol silver trifluoroacetate as a matrix. Elemental analyses were performed by the University of Illinois Microanalytical service Laboratory using a Perkin-Elmer Model P2000 analyzer. Gel permeation chromatography (GPC) was conducted on a Waters 486 chromatograph in THF using STYRAGEL® HMW 2 and STYRAGEL® HMW 6E columns, 510 pumps, 486 UV-detector, and 410 RI detector.
General Procedure for Esterification Reactions
(divergent synthesis of dendritic block D of DRC Compound (1))

The esterification reactions were performed on a scale of about 4 to about 12 grams (g). In these reactions, a mixture of the diblock R-C rodcoil (1 equivalent), 3,5-bis(tert-butyldimethylsiloxyl)benzoic acid (1 equivalent), and DPTS (1 equivalent) was dissolved in methylene chloride (CH$_2$Cl$_2$), and the resulting mixture was stirred under nitrogen. DIPE (1 equivalent) was added to the stirred mixture via syringe, and the reaction was allowed to proceed, with stirring, for 3 hours. Urea impurities then were removed by precipitation, i.e., by adding the concentrated reaction mixture into methanol (3 times). The precipitate was dissolved in CH$_2$Cl$_2$, and the crude product, i.e., a silyl-protected DRC compound (1) was purified by flash chromatography as outlined below.

General Procedure for Silyl Deprotection
(divergent synthesis of the dendritic block D of DRC compound (1))

These reactions also were performed on a scale of about 4 to about 12 g. Silyl-protected DRC compound (1) (1 equivalent), as prepared above, was dissolved in THF in a plastic vessel. Hydrofluoric acid (49% aq. solution) was added to the resulting solution via syringe (10 equivalents). The resulting reaction mixture was stirred, and allowed to react for several hours (e.g., about 2 to about 8 hours). The reaction then was diluted with CH$_2$Cl$_2$,
and quenched with a saturated sodium bicarbonate solution. The resulting mixture was washed several times with water, and the crude product, i.e., DRC compound (1), was purified by flash chromatography, as outlined below.

Preparation of Isoprene Oligomer
(C block of DRC Compound (1))

Benzene (100 mL) and THF (20 mL) were added to a flask, followed by the addition of n-butyl lithium (n-BuLi, 1 equivalent), and finally the addition of isoprene (9 equivalents). The resulting reaction mixture was stirred for 30 minutes, then quenched by bubbling ethylene oxide through the solution for about 15 minutes, followed by addition of 10 mL (milliliters) of 3 N HCl/THF (1/2 weight ratio). The solvents then were removed by rotatory evaporation. The resulting crude product was purified by flash chromatography by eluting with 50% \( \text{CH}_2\text{Cl}_2/\text{hexane} \), and gradually increasing to 100% \( \text{CH}_2\text{Cl}_2 \), to yield the hydroxy-terminated isoprene oligomer (i.e., block C) as a colorless liquid.

Yield: 65% \( ^1\text{H NMR} \) (500 MHz, THF-\( \text{d}_4 \)) \( \delta \) 0.5-2.8 (br m, 7OH aliphatic), 3.61 (br m, 2H, \( \text{CH}_2\text{OH} \)), 4.5-5.2 (br m, 14H vinyl); FD-MS \( m/z \) 770; (Found: C, 85.57; H, 12.42. Calc. for \( \text{C}_{51}\text{H}_{86}\text{O}_2 \): C, 83.83; H, 11.78%).
Preparation of 4'-tert-Butyldimethylsilyloxy-4-(dimethylsilyloxycarboxylate)biphenyl (Reactant A)

A dry flask was charged with 4'-hydroxy-4-biphenylylcarboxylic acid (1 equivalent), imidazole (2.2 equivalent), and N,N-dimethylformamide (DMF). After stirring the resulting mixture for about 10 minutes, tert-butyldimethylsilylchloride (2.2 equivalents) was added to the mixture. The resulting solution was stirred overnight at room temperature, then diluted with CH₂Cl₂ and washed several times with saturated aqueous sodium bicarbonate and water. The organic layers then were dried over MgSO₄, filtered, and the solvent was removed by rotary evaporation. The named product was purified by flash chromatography by eluting with CH₂Cl₂ to yield a colorless liquid. Yield: 91%. ¹H NMR (500 MHz, THF-d₈) δ 0.26 (br s, 12H, OSi(CH₃)₂C(CH₃)₃), 1.04 (br s, 18H, OSi(CH₃)₂C(CH₃)₃), 6.96 (d, 2H, J=8.5 Hz, Ar' H), 7.60 (d, 2H, J=8.6 Hz, Ar' H), 7.69 (d, 2H, J=8.6 Hz, Ar' H), 8.16 (d, 2H, J=8.4 Hz, Ar' H); FD-MS m/z 442 (M⁺). (Found: C, 67.72; H, 8.71; Si, 12.35. Calc. for C₂₅H₁₆O₂Si₂: C, 67.87, H, 8.60; Si, 12.67%).

Preparation of 4'-tert-Butyldimethylsilyloxy-4-biphenylylcarboxylic acid (Reactant B)

The named compound was prepared from the above Reactant A by standard methods and was purified by flash chromatography by eluting with 30% THF/CH₂Cl₂, and recrystallization from 70% hexane/-CH₂Cl₂, to yield the named compound as white crys-
tals. Yield: 87%. $^1$H NMR (500 MHz, THF-$d_8$) δ 0.24 (s, 6H, OSi(CH$_3$)$_2$C(CH$_3$)$_3$), 1.02 (s, 9H, OSi(CH$_3$)$_2$C(CH$_3$)$_3$), 6.94 (d, 2H, J=8.6 Hz, Ar'H), 7.58 (d, 2H, J=8.6 Hz, Ar'H), 7.66 (d, 2H, J=8.4 Hz, Ar'H), 8.06 (d, 2H, J=8.4 Hz, Ar'H); FD-MS m/z 328 (M$^+$); (Found: C, 70.12; H, 7.55; Si, 8.39. Calc. for C$_{19}$H$_{24}$O$_7$Si: C, 69.51; H, 7.32; Si, 8.54%).

Preparation of 1-(tert-Butyldimethylsilylcarboxy)-3,5-bis(tert-butyldimethylsilyloxy)benzene (Reactant C)

3,5-Dihydroxybenzoic acid (1 equivalent) and imidazole (3.5 equivalent) were dissolved in DMF under a nitrogen atmosphere. tert-Butyldimethylsilyl chloride (3.5 equivalents) was added, and the resulting solution was stirred overnight. The reaction mixture was diluted with CH$_2$Cl$_2$, washed with water, and dried over MgSO$_4$. The solvent was removed by rotary evaporation, and the product was purified by flash chromatography (CH$_2$Cl$_2$) to yield the named compound as a colorless liquid. Yield: 96%. $^1$H NMR (500 MHz, THF-$d_8$) δ 0.23 (s, 12H, OSi(CH$_3$)$_2$C(CH$_3$)$_3$), 0.47 (s, 6H, COOSi(CH$_3$)$_2$C(CH$_3$)$_3$), 1.01 (br s, 27H, Si(CH$_3$)$_2$C(CH$_3$)$_3$), 6.60 (t, 1H, J=2.2 Hz, Ar"H), 7.22 (d, 2H, J=2.4 Hz, Ar"H); $^{13}$C NMR (125 MHz, THF-$d_8$) δ -4.31, 0.17, 18.98, 19.19, 26.17, 115.65, 117.31, 133.97, 157.96, 167.40; FD-MS m/z 496 (M$^+$); (Found: C, 60.63; H, 9.74; Si, 16.69. Calc. for C$_{25}$H$_{48}$O$_7$Si$_3$: C, 60.48; H, 9.68; Si, 16.94%).
Preparation of 3,5-bis(tert-Butyldimethylsilyloxy)-benzoic acid (Reactant D)

1-(tert-Butyldimethylsilylcarboxy)-3,5-bis(tert-butyldimethylsilyloxy)benzene, i.e., Reactant C, (18 g) was dissolved in 300 mL of a THF/-H2O/ACOH mixture (50:10:40 by volume), and the resulting mixture was stirred for 24 hours. The reaction mixture then was concentrated under reduced pressure, and precipitated in 500 mL of ethanol. The precipitate was washed several times with a saturated aqueous sodium bicarbonate solution, water, and then purified by flash chromatography eluting with CH2Cl2 and gradually increasing to 40% THF/CH2Cl2 and recrystallization from 50% hexanes/CH2Cl2 to yield the named compound as white needle-like crystals. Yield: 80%. 1H NMR (500 MHz, THF-d8) δ 0.22 (s, 12H, OSi(CH3)2C(CH3)₃), 1.00 (s, 18H, Si(CH3)2C(CH3)₃), 6.54 (t, 1H, J=2.2 Hz, Ar"H), 7.14 (d, 2H, J=2.4 Hz, Ar"H); 13C NMR (125 MHz, THF-d8) δ -4.29, 18.88, 26.10, 115.47, 117.09, 133.80, 157.41, 167.21; FD-MS m/z 382 (M⁺); (Found: C, 59.73; H, 8.99; Si, 14.61. Calc. for C31H20O₄Si₂; C, 59.69; H, 8.90; Si, 14.65%).

Preparation of Diblock Polymer Containing R and C Blocks

The diblock polymer was prepared from esterification of the hydroxy-functionalized isoprene oligomer and Reactant B (4-tert-butyldimethylsilyloxy-4-biphenylcarboxylic acid) by the above-described general esterification procedure. The
reaction product was purified by flash chromatography by eluting with CH₂Cl₂ to yield a silyl-protected diblock RC polymer as a colorless liquid. Yield: 69%. ¹H NMR (500 MHz, THF-d₈) δ 0.23 (s, 6H, OSi-(CH₃)₃C(CH₃)₃), 0.5-2.8 (br m, 80H aliphatic), 4.29 (br m, 2H, CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.95 (d, 2H, J=8.6 Hz, Ar'H), 7.55 (d, 2H, J=8.4 Hz, Ar'H), 7.67 (d, 2H, J=8.4 Hz, Ar'H), 8.04 (d, 2H, J=8.5 Hz, Ar'H); MALDI-MS m/z 1100; GPC (254 nm, THF) PDI=1.09, M₉=1520.

A diblock RC polymer was prepared from the silyl protected diblock RC polymer by the above-described general silyl deprotection method, and was purified by flash chromatography by eluting with 5% THF/CH₂Cl₂ to yield a diblock RC polymer as a colorless liquid. Yield: 95%. ¹H NMR (500 MHz, THF-d₈) δ 0.5-2.8 (br m, 70H aliphatic), 4.26 (br m, 2H, CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.83 (d, 2H, J=8.4 Hz, Ar'H), 7.52 (d, 2H, J=8.3 Hz, Ar'H), 7.65 (d, 2H, J=8.2 Hz, Ar'H), 8.02 (d, 2H, J=8.5 Hz, Ar'H), 8.45 (s, 1H, Ar'OH); MALDI-MS m/z 990; GPC (254 nm, THF) PDI=1.07, M₉=1380.

The above two esterification and silyl deprotection reactions were identically performed, in sequence, two additional times to complete synthesis of the diblock RC polymer. The complete reaction sequence provided a diblock RC polymer containing an oligomer of nine isoprene units covalently bound to an oligomer of three biphenyl compounds. The individual products resulting from addition of the second and third biphenyl compounds to the isoprene oligomer are summarized below.
The second biphenyl compound was added to the diblock RC polymer by the previously described esterification reaction, and was purified by flash chromatography by eluting with CH₂Cl₂ to yield a colorless liquid. Yield: 90%. ¹H NMR (500 MHz, THF-d₆) δ 0.25 (s, 6H, OSi(CH₃)₂C(CH₃)₃), 0.5-2.8 (br m, 80H aliphatic), 4.30 (br m, 2H, CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.97 (d, 2H, J=8.6 Hz, Ar'H), 7.40 (d, 2H, J=8.4 Hz, Ar'H), 7.62 (d, 2H, J=8.6 Hz, Ar'H), 7.80 (m, 6H, Ar'H), 8.11 (d, 2H, J=8.5 Hz, Ar'H), 8.22 (d, 2H, J=8.4 Hz, Ar'H); MALDI-MS m/z 1300; GPC (254 nm, THF) PDI=1.07, Mₙ=1760.

The above compound, in turn, was silyl deprotected by the previously described silyl deprotection reaction, and was purified by flash chromatography eluting with 5% THF/CH₂Cl₂ to yield a tacky solid. Yield: 87%. ¹H NMR (500 MHz, THF-d₆) δ 0.5-2.8 (br m, 70H aliphatic), 4.30 (br m, 2H, CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.87 (d, 2H, J=8.6 Hz, Ar'H), 7.38 (d, 2H, J=8.4 Hz, Ar'H), 7.59 (d, 2H, J=8.6 Hz, Ar'H), 7.77 (m, 6H, Ar'H), 8.09 (d, 2H, J=8.6 Hz, Ar'H), 8.21 (d, 2H, J=8.4 Hz, Ar'H), 8.51 (s, 1H, Ar'OH); MALDI-MS m/z 1180; GPC (254 nm, THF) PDI=1.08, Mₙ=1610.

A third biphenyl compound was added to complete the synthesis of diblock RC polymer by esterifying the above compound. The resulting esterification product was purified by flash chromatography by eluting with 7% THF/CH₂Cl₂ to yield a white solid. Yield: 76%. ¹H NMR (500 MHz, THF-d₆) δ 0.26 (s, 6H, OSi(CH₃)₂C(CH₃)₃), 0.5-2.8 (br m, 80H aliphatic), 4.30 (br m, 2H, CH₂OCOAr'), 4.5-5.2 (br
m, 14H vinyl), 6.98 (d, 2H, J=8.6 Hz, Ar'H), 7.41 (m, 4H, Ar'H), 7.66 (d, 2H, J=8.6 Hz, Ar'H), 7.80 (m, 6H, Ar'H), 7.85 (d, 2H, J=8.7 Hz, Ar'H), 7.89 (d, 2H, J=8.6 Hz, Ar'H), 8.11 (d, 2H, J=8.5 Hz, Ar'H), 8.24 (d, 2H, J=8.6 Hz, Ar'H), 8.29 (d, 2H, J=8.4 Hz, Ar'H); MALDI-MS m/z 1490; GPC (254 nm, THF) PDI=1.07, Mₙ=1970.

The above compound was silyl deprotected by the previously described method to provide the diblock RC polymer, which was purified by flash chromatography by eluting with 35% THF/CH₂Cl₂ to yield a white solid. Yield: 72%. ¹H NMR (500 MHz, THF-d₈) δ 0.5-2.8 (br m, 70H aliphatic), 4.30 (br m, 2H, CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.87 (d, 2H, J=8.6 Hz, Ar'H), 7.40 (m, 4H, Ar'H), 7.59 (d, 2H, J=8.6 Hz, Ar'H), 7.77 (m, 6H, Ar'H), 7.82 (d, 2H, J=8.6 Hz, Ar'H), 7.87 (d, 2H, J=8.4 Hz, Ar'H), 8.10 (d, 2H, J=8.5 Hz, Ar'H), 8.22 (d, 2H, J=8.4 Hz, Ar'H), 8.29 (d, 2H, J=8.3 Hz, Ar'H), 8.53 (s, 2H, Ar'OH); MALDI-MS m/z 1380; GPC (254 nm, THF) PDI=1.07, Mₙ=1820.

**Addition of Dendritic Block D to Diblock RC**

The diblock RC prepared above was reacted with Reactant D (3,5-bis(tert-butyldimethyldisilyloxy)benzoic acid), by the above-described general esterification method, and the resulting product was purified by flash chromatography by eluting with 7% THF/CH₂Cl₂ to yield a white solid. Yield: 89%. ¹H NMR (500 MHz, THF-d₈) δ 0.27 (s, 12H, OSi(CH₃)₂C-(CH₃)₃), 0.5-2.8 (br m, 88H aliphatic), 4.31 (br m,
2H, CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.70 (t, 1H, J=2.2 Hz, Ar''H), 7.32 (d, 2H, J=2.0 Hz, Ar''H), 7.40 (m, 6H, Ar'H), 7.78 (m, 4H, Ar'H), 7.84 (d, 4H, J=8.4 Hz, Ar'H), 7.88 (d, 4H, J=8.2 Hz, Ar'H), 8.10 (d, 2H, J=8.5 Hz, Ar'H), 8.29 (d, 4H, J=8.1 Hz, Ar'H); MALDI-MS m/z 1740; GPC (254 nm, THF) PDI=1.08, Mₙ=2190.

The above product was silyl deprotected by the above-described general silyl deprotection method, and the resulting product was purified by flash chromatography by eluting with 15% THF/CH₂Cl₂ to yield a white solid. Yield: 77%. ¹H NMR (500 MHz, THF-d₈) δ 0.5-2.8 (br m, 70H aliphatic), 4.30 (br m, 2H, CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.49 (t, 1H, J=2.2 Hz, Ar''H), 7.08 (d, 2H, J=2.4 Hz, Ar''H), 7.40 (m, 6H, Ar'H), 7.78 (m, 4H, Ar'H), 7.82 (d, 4H, J=8.6 Hz, Ar'H), 7.86 (d, 4H, J=8.6 Hz, Ar'H), 8.09 (d, 2H, J=8.5 Hz, Ar'H), 8.29 (d, 4H, J=8.3 Hz, Ar'H), 8.52 (s, 2H, Ar''OH); MALDI-MS m/z 1520; GPC (254 nm, THF) PDI=1.08, Mₙ=2050.

The above silyl deprotected compound was reacted with Reactant D (3,5-bis(tert-butyldimethylsilyloxy)benzoic acid) according to the above-described general esterification method, and the resulting product was purified by flash chromatography by eluting with CH₂Cl₂ to yield a white solid. Yield: 89%. ¹H NMR (500 MHz, THF-d₈) δ 0.26 (s, 24H, OSi(CH₃)₂C(CH₃)₃), 0.5-2.8 (br m, 106H aliphatic), 4.30 (br m, 2H, CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.68 (t, 2H, J=2.3 Hz, Ar''H), 7.33 (d, 4H, J=2.3 Hz, Ar''H), 7.42 (m, 6H, Ar'H), 7.60 (t, 1H, J=2.2 Hz, Ar''H), 7.79 (m, 4H, Ar'H), 7.85 (d,
4H, J=8.6 Hz, Ar'H), 7.90 (d, 4H, J=8.4 Hz, Ar'H), 8.04 (d, 2H, J=2.2 Hz, Ar"H), 8.10 (d, 2H, J=8.5 Hz, Ar'H), 8.29 (d, 4H, J=8.0 Hz, Ar'H); MALDI-MS m/z 2250; GPC (254 nm, THF) PDI=1.08, M_w=3060.

The above silyl protected product was silyl deprotected by the above-described general silyl deprotection method, and resulting reaction product was purified by flash chromatography by eluting with CH₂Cl₂ and gradually increasing to 10% THF/CH₂Cl₂ to yield the DRC compound of structural formula (1) as a white solid. Yield: 78%. ¹H NMR (500 MHz, THF-d₈) δ 0.5-2.8 (br m, 70H aliphatic), 4.30 (br m, 2H, 'CH₂OCOAr'), 4.5-5.2 (br m, 14H vinyl), 6.51 (t, 2H, J=2.2 Hz, Ar"H), 7.10 (d, 4H, J=2.4 Hz, Ar"H), 7.42 (m, 6H, Ar'H), 7.58 (t, 1H, J=2.2 Hz, Ar"H), 7.79 (m, 4H, Ar'H), 7.85 (d, 4H, J=8.6 Hz, Ar'H), 7.89 (d, 4H, J=8.4 Hz, Ar'H), 8.01 (d, 2H, J=2.2 Hz, Ar"H), 8.10 (d, 2H, J=8.5 Hz, Ar'H), 8.29 (d, 4H, J=8.1 Hz, Ar'H), 8.59 (s, 4H, Ar"OH); ¹³C NMR (125 MHz, THF-d₈) δ 14.45, 19.23, 23.54, 24.98, 28.08, 30.00, 32.77, 40.24, 43.03, 45.82, 63.43, 65.22, 67.91, 108.91, 108.97, 109.01, 112.3, 121.57, 123.18, 123.25, 127.67, 127.90, 128.98, 129.09, 129.14, 129.42, 130.82, 131.47, 131.59, 132.03, 138.07, 146.06, 152.52, 152.61, 152.93, 160.06, 164.03, 164.97, 166.21; MALDI-MS m/z 1790; GPC (254 nm, THF) PDI=1.08, M_w=2340.

The DRC compounds of the present invention have the ability to impart order to organic media, for example, organic solvents and organic monomers. Ordering of the organic solvent or monomer is demonstrated by the formation of a birefringent gel by the addition of about 0.05% to about 2%, by weight.
of the organic media, of a DRC compound to the organic media. In the case of an organic monomer, the birefringent gel can be subjected to a polymerization reaction to form a birefringent polymer.

Surprisingly, the birefringent polymer can be melted and retain its birefringence, then the birefringent melt can be formed into a birefringent article of manufacture, like a fiber. The birefringent polymer retains its birefringent property even after several melt cycles, and, in each cycle, the melt exhibits liquid crystalline-like properties. This is a totally unexpected property for a polymer composite comprising 98% or greater polystyrene.

Alternatively, a birefringent gel containing DRC molecules and an organic monomer can be prepared in a desired, predetermined shape. This birefringent gel then can be subjected to polymerization conditions to provide a birefringent article of manufacture. For example, a birefringent gel can be spun and formed into a fiber after polymerization, or the birefringent gel can be prepared in a form, which, after polymerization, provides an article of manufacture in the shape of the form.

To illustrate the surprising properties provided by a DRC compound of the present invention, the DRC compound of structural formula (1) was dissolved in dichloromethane to form a dilute 1 weight % solution of DRC compound (1). The resulting solution undergoes spontaneous gelation to form a soft solid having a blue-violet hue.

In particular, the DRC compound of structural formula (1) and dichloromethane were added to a capped vessel, and the resulting mixture was
heated to 70-80°C. When dissolution of DRC compound (1) was complete, a viscous, blue solution formed, which gelled within several minutes at 70°C. The vessel then was cooled to room temperature.

The resulting gel was optically transparent and had blue-violet color. Neither phase separation nor precipitation was observed in the gels, and the gels remained stable for extended periods of time. Temperature-induced melting of the gels did not occur, even when the sealed vessel containing the gel was heated to 100°C (i.e., 60°C above the boiling point of dichloromethane), at which point the vapor pressure of CH₂Cl₂ destroyed the vessel.

When the concentration of DRC compound (1) in CH₂Cl₂ was decreased to 0.3 weight %, a blue-violet gel also formed. At a concentration below 0.3%, by weight, the soft gel that formed could no longer support its own weight upon inversion of the vial containing the gel.

Birefringent gel formation is illustrated in Fig. 1. Fig. 1A contains photographs of a series of inverted vials showing the formation of CH₂Cl₂ gels containing 0.3% to 1.5%, by weight, DRC compound, and showing the flow of a gel prepared using 0.2 weight % of DRC compound (1) in dichloromethane. The % of DRC compound in each gel is indicated on the vials. All the gels in Fig. 1A were birefringent when observed under cross polarizers in an optical microscope, and most importantly, upon heating, melting of the gel is not observed in a sealed vessel, even at temperatures well above the boiling point of the solvent. Thus, the gel structure illustrated in Fig. 1 is thermally irreversible, con-

Birefringent gels also can be formed by adding a DRC compound to an organic monomer in an amount of about 0.05% to about 2%, by weight of the organic monomer. The organic monomer can be a liquid or a gas. Typically, the DRC compound is added to the organic monomer in an amount of about 0.1% to about 1.5%, and preferably about 0.25% to about 1%, by weight. Birefringent gels containing 0.3% to 2%, by weight of the DRC compound, have sufficient strength to support their own weight.

For example, a birefringent gel can be formed by introducing a DRC compound (0.2 g) and styrene (20 g) into a capped vessel, followed by heating the vial in an oil bath for 10-15 minutes at about 100°C until all the DRC compound was dissolved. The resulting solution was rapidly cooled to room temperature, and the birefringent gel formed within several minutes. The gel was aged for one day at room temperature, then the capped vial was placed in a heating chamber at 110°C under nitrogen
atmosphere for 48 hours. Under these conditions, the soft gel was transformed into solid polymer composite, which had the characteristic blue-violet hue of a birefringent material and was transparent to visible light.

Therefore, when birefringent gels containing a DRC compound and styrene are heated to about 100°C, polymerization of styrene occurs without any indication of a disruption of the gel structure, and the resulting hard polymer composite retains the same blue-violet hue of the gel. The birefringent polystyrene was examined by size exclusion chromatography (SEC), which indicated an average $M_w$ of about 240,000, and a relatively low polydispersity index of about 1.9.

An analogous procedure was used to prepare crosslinked birefringent polystyrene. DRC compound (1) (10 mg), styrene (1 g), divinylbenzene (50 mg), and benzoin ethyl ether (50 mg) were placed in a capped vessel, then heated at 100°C until all solid materials were dissolved (about 10 minutes). The vial was rapidly cooled to room temperature, then was irradiated with UV light (365 nm) at 20°C for 36 hours. The properties of the resulting crosslinked polymer were very similar to those of the birefringent uncrosslinked polystyrene composite, i.e., SAXS signal at 100 Å, birefringence under crossed polarizers up to 300°C, and macroscopic orientation of the stressed fibers.

Fig. 1(B and C) contain photographs of three polystyrene specimens, each polymerized under the same conditions. Fig. 1(B) contains photographs of free-standing specimens. Fig. 1(C) contains
photographs of the three specimens laying on a table.

The specimen on the left of Fig. 1 (B and C) is pure polystyrene. The middle specimen is a gel-derived polystyrene containing 1%, by weight, of the DRC compound of structural formula (1). The right specimen is a gel-derived from poly(2-ethylhexyl methacrylate), a rubber-like material at room temperature, containing 1%, by weight, of the DRC compound of structural formula (1). The photographs of Fig. 1 (B and C) reveal the optical transparency of all samples, and a wavelength filtering effect at the bottom of the gel-derived samples, which is not observed in the pure polystyrene sample. The polystyrene and poly(2-ethylhexyl methacrylate) containing the DRC are birefringent, and thus have retained some order after polymerization. The polystyrene composites containing the DRC compound (1) exhibited birefringence under crossed polarizers and gave small angle X-ray (SAXS) peaks with a primary d-spacing of 100 Å corresponding to double the length of the DRC compound of structural formula (1). This illustrates that the DRC molecules (1) form a bimolecular species wherein the D blocks of the DRC molecules are associated, and the C blocks are at the termini of the bimolecular species (see Fig. 4).

Nuclear magnetic resonance (NMR) reveals a striking change in rotational mobility only for protons present in the aromatic segments of the DRC compound after gelation of an organic medium. Fig. 2 contains NMR spectra of a THF solution of the DRC compound of structural formula (1) (top) and of the DRC compound (1) in a dichloromethane gel (bottom).
A molecular representation of the DRC compound of structural formula (1) is shown on the right of Fig. 2.

Specifically, Fig. 2 shows the disappearance of aromatic resonances in the gel formed in dichloromethane (bottom). The aromatic resonances are clearly resolved in the NMR spectra of a solution of DRC compound (1) in tetrahydrofuran (top). All three types of protons (aromatic, vinyl, and aliphatic) generate signals in THF solutions because the DRC molecules can freely rotate in the absence of aggregation. The NMR signals that disappeared after gelation correspond to aromatic protons from both the dendritic (D) and rod (R) segments of DRC compound (1). The absence of these NMR resonances indicates that a drastic decrease in motion has occurred, which results in nonaveraging of magnetic anisotropies. On the other hand, protons from the flexible oligoisoprene coil (C) segment still generate intense, but somewhat broadened, signals after gelation. Similar observations were made in NMR spectra of styrene-based gels of DRC compound (1). Based on such evidence, it was concluded, but not relied upon herein, that aggregation of DRC molecules is mediated by aromatic units, and that aggregation is responsible for the birefringent gelation of nonpolar solvents, like CH₂Cl₂. In contrast, oligoisoprene segments (blocks C) retain their rotational freedom in what is theorized to be a solvated self-assembled structure.

A surprising feature observed after polymerization of a styrene-based birefringent gel is the presence of uniform birefringence when polymer
samples are viewed between crossed polarizers in an optical microscope. For example, Fig. 3(A) contains a small angle X-ray pattern of a gel-derived polystyrene containing 1 weight % of DRC compound (1), and Fig. 3(B and C) contain optical micrographs between crossed polarizers showing the birefringent texture of polystyrene containing 1 weight % DRC compound (1) at 100°C (B) and 250°C (C). If the polymer did not exhibit birefringence, Fig. 3(B) and Fig. 3(C) would appear black. Polarized optical microscopy at elevated temperatures revealed a texture similar to that observed in liquid crystals and which was present until the isotropization point was reached at 310°C.

The bright optical texture observed at the glass transition temperature (100°C) of polystyrene indicates a highly anisotropic medium (Fig. 3B). Very surprisingly, when the polystyrene composite is heated well above the glass transition temperature (250°C), and flow is observed, birefringence still remains. Importantly, the homogeneity of the optical texture shows the absence of macrophase separation. The self-assembled structure is suggested to be an aggregation of DRC molecules, in the form of ribbons of bimolecular DRC species.

In contrast, when the same experiment is performed using a nondendritic analog of the DRC compound 1, i.e., the diblock RC compound, a biphasic texture is observed revealing readily visible birefringent droplets of diblock RC compound imbedded in an isotropic polystyrene matrix. This macrophase separated solid is a turbid, opaque material lacking the transparency of the gel-derived samples.
This is illustrated in Fig. 4, which contains photographs of a polystyrene composite containing 1 weight % of DRC compound (1), and the biphasic opaque material containing 1 weight % of diblock RC molecules. A molecular representation of rod-dendron segments of DRC compound (1) (left in Fig. 4) shows frustrated packing in the x-y plane due to the presence of bulky dendritic fragments. The close packing of the rod segments in diblock RC molecules (right in Fig. 4) is not prevented, which is why diblock RC molecules can strongly aggregate via \( \pi-\pi \) stacking of biphenyl units forming two-dimensional assemblies within x-y plane. It has been suggested that a frustrated long-range aggregation in two dimensions among dendritic molecules plays an important role in this very unexpected behavior.

Small angle X-ray scattering of the polymerized birefringent gel also reveals a Bragg reflection with characteristic spacing of about 10.7 nm (Fig. 3A). The force field minimized length of average-sized DRC molecules is about 6.5 nm (nanometers), and, therefore, the \( d \)-spacing observed is consistent with bilayer packing of dendron rodcoils to form a bimolecular species. The observed spacing is consistent with head-to-head (i.e., D block to D block) packing of DRC molecules (Fig. 4), and interdigitation of the flexible oligoisoprene C block segments. This bilayer is theorized to be the main structural species, and also is the fundamental bimolecular species causing medium gelation. Surprisingly, gels formed in dichloromethane and styrene monomer do not produce any small angle diffraction. At the same time, it was previously stated that
based on NMR evidence, DRC molecules are aggregated in the gel state. This suggests that in the gel, bimolecular species on the order of 10 nm form long separated strings, and, therefore, lack the necessary coherence to observe X-ray diffraction.

Fibers were drawn from a birefringent melt of the birefringent polymer, and surprisingly, the solid fiber not only maintained its birefringence, but also revealed macroscopic orientation of the molecular DRC scaffold by small angle X-ray diffraction (Figs. 5D and 5F). Similar fibers drawn from a pure polystyrene melt show almost no birefringence, and do not reveal evidence of molecular orientation by small angle X-ray diffraction (Figs. 5C and 5E).

Overall, Fig. 5 contains a wide-angle X-ray diffraction pattern collected from a pure polystyrene fiber (A) and a fiber of polystyrene containing 1 weight % of DRC compound (1) (B); small-angle X-ray diffraction pattern collected from the pure polystyrene fiber (C) and the fiber of scaffolded polystyrene containing 1 weight % of DRC compound (1) (D); and an optical micrograph between crossed polarizers showing the melt-drawn fibers of pure polystyrene (E) and a polystyrene containing 1 weight % of DRC compound (1) (F).

Wide angle x-ray patterns also were analyzed to estimate the extent of polystyrene chain orientation in samples containing a DRC compound of the present invention, and in samples free of a DRC compound. In the analysis, Hermans orientation factor \( f \),

\[
f = \frac{1}{2} (3 \cos^2 \theta - 1),
\]
wherein $\theta$ is the angle between the fiber axis and chain segments and $(\cos^2\theta)$ is the average cosine squared of $\theta$, was calculated. The calculation of $f$ revealed a significantly higher degree of orientation for polystyrene chains in DRC containing polystyrene at all draw ratios, $\lambda$, used. This unexpected result is illustrated in Fig. 8, wherein the lower plot relates polystyrene, and the higher plot (i.e., a greater $f$) relates to polystyrene containing 1% by weight of DRC compound (1) of the present invention.

This data suggests that a network of nanoribbons acts as a highly dispersed scaffold to more easily orient the surrounding molecular matrix under the influence of mechanical force. The exact scaffolding mechanism is unknown at this time, but one hypothesis is that polymer chains entangle with the orientable scaffold. Alternatively, short range orientation (i.e., unfolding) of polymer chains by the nanoribbons can be occurring even in the mechanically undeformed state.

Ultramicrotomed sections of the polymerized birefringent gel were analyzed by transmission electron microscopy (TEM) after staining with osmium tetroxide ($\text{OsO}_4$). TEM samples were cut using a Riechert-Jung Ultracut S microtome equipped with a diamond knife at an average thickness of 75-80 nm. The sections were transferred to holey carbon coated TEM grids, and then stained with $\text{OsO}_4$ vapors for 2 hours, which selectively stains the unsaturated double bonds in the oligoisoprene C block of the DRC compound.
Fig. 6 is a typical electron micrograph of a cross section of a polymerized birefringent gel containing a small percentage of divinylbenzene to crosslink the polymer matrix. Small amounts of divinylbenzene crosslinker, typically about 2 weight % by weight of the monomer, were used to prepare the samples investigated by TEM. Divinylbenzene was used to maximize conversion of styrene monomer to polymer, and to eliminate contributions of residual styrene to the staining contrast.

Fig. 6, therefore, is a transmission electron micrograph, at high magnification, of a thin film (75 nm thick) ultramicrotomed from a polystyrene composite containing 1 weight % of DRC compound (1) showing a domain of DRC molecules (A), a matrix of polystyrene (B), and circular arched features (C) which are theorized to be bimolecular strands of DRC molecules passing through the polystyrene matrix perpendicular to the cutting plane. The contrast in the TEM of Fig. 6 is produced by osmium tetroxide which selectively stains carbon-carbon double bonds in the oligoisoprene segment of the DRC molecules.

In particular, the elongated dark feature labeled A in Fig. 6 comprises thin black lines, which are theorized to be a domain of aggregated DRC molecules. Oligoisoprene blocks in the DRC molecules are the only stainable segments of the polymers, and, therefore, the light gray background B is the continuous matrix of crosslinked polystyrene. The spacing of dark lines within feature A is roughly 10 nm, which is commensurate with the characteristic d-spacing observed in X-ray experiments. The image in Fig. 6 confirms the bimolecular ar-
rangement of DRC molecules in the polymer matrix. The oligoisoprene segments are spatially isolated by a stain-resistant region that appears darker than the matrix, suggesting that this region contains densely-packed biphenyl segments. The lack of continuity of the black lines implies that the aggregated DRC molecules meander through the matrix in three dimensions.

One important feature of the image in Fig. 6 is the small, circularly-shaped dark objects dispersed throughout and labeled as C. If an arbitrary slice is cut from a random three-dimensional network, then some strands pierce the cross section and others lie in the plane of the cross section. It is theorized that the circular features in the image are bimolecular strands of DRC molecules passing perpendicular to the cutting plane. Furthermore, the circular features have modes of darkness suggesting the strands do not have cylindrical symmetry. The distance between the arcs in these features again is 10 nm, which matches the observed spacing in A domains. The fact that thin black lines in the observed domains match the oligoisoprene block dimensions (about 3 nm) is strong evidence for the noncylindrical nature of the strands. Finally, a percent area analysis of various images agrees with a 1 weight % fraction of DRC compound in the polymer composite.

The above data makes it clear that a self-assembled structure formed by DRC molecules is highly dispersed throughout the organic medium, either a solvent or polymer. The ability of such a small amount of DRC compound to gel a much larger weight
fraction of an organic medium suggests that the DRC molecules act as a scaffold. Specifically, the ratio of organic medium molecules to DRC molecules can be as high as about 7,000:1, which implies an enormous contact surface area between the DRC molecules and the organic medium, and suggests that a nanoscaffold of aggregated DRC molecules weaves throughout the medium. It is surprising and unexpected that such a small amount of DRC compound provides for the retention of optical birefringence in a monomeric soft gel, a hard polymer matrix, and a macromolecular melt of the polymer matrix.

The presence of a 10 nm periodicity in the polymer matrix is clear in the micrograph of the polymeric solid, which shows slightly segregated structures of the nanoscaffold. The absence of such a periodicity in the unpolymerized birefringent gel suggests the DRC nanoscaffold is highly dispersed throughout the gel, and, therefore, lacks a coherent scattering power to reveal its characteristic dimension. In fact, the presence of single DRC strands is observed in the electron micrograph of the polymerized system. Polymerization of the gel generates sufficient segregation of scaffold structures to generate sufficient coherent scattering and produce a periodicity window.

In view of the data presented above, it was concluded, but not relied upon herein, that the effects demonstrated by the present DRC compounds are attributed to an aggregated, nanoscaffold structure that effectively is a semiflexible bimolecular ribbon formed by DRC molecules. The existence of a ribbon structure matches the observed X-ray period-
icity and the staining pattern observed by electron microscopy. The semiflexibility of the DRC ribbons weaving through the gel or polymer matrix is supported by the meandering of the observed nanostructures. Fig. 7 sets forth a schematic molecular representation of the bimolecular ribbon formed by self-assembly of DRC molecules. Fig. 7 illustrates the nanoscaffold and shows how nanoscaffold dimensions can be explained from the identity of the DRC molecules in the nanoscaffold.

In particular, the area of contact of scaffold material with the polymer matrix is estimated to be about 16 m²/cm³ in a system containing 1 weight % of the self-assembling DRC compound in the polymer matrix. This estimate is based on first calculating the total number of DRC molecules of structural formula (1) contained in 1 cm³ of the styrene gel on the basis of the average molecular weight of DRC determined by mass spectrometry (i.e., about 1700 g/mole). Using that number \( N \), the length and the surface of a hypothetical bimolecular ribbon with a width 10 nm (based on SAXS and TEM experiments), and the lateral spacing between the DRC molecules of 0.45 nm (based on wide-angle X-ray diffraction), was estimated. The length \( L \) of the ribbon 1 cm³ of 1 weight % DRC compound in a gel was calculated as

\[
L = \frac{N \cdot d}{m \cdot N \cdot d} = \frac{10^{-2} \cdot 6.02 \cdot 10^{21} \cdot 4.5 \cdot 10^{-10}}{2 \cdot MW} \cdot \frac{1}{2 \cdot 1700} = 7.97 \times 10^8 \text{ m},
\]

wherein \( N \) is the total number of DRC molecules; \( d \) is the primary distance between the DRC molecules along
the axis of the ribbon; m is the mass of the DRC compound; \( N_A \) is Avogadro's number; \( MW \) is the average molecular weight of the DRC compound. The surface area of the ribbon then was estimated as

\[ S = 2 \cdot L \cdot D = 2 \cdot 7.97 \cdot 10^4 \cdot 10^4 = 15.94 \text{m}^2, \]

wherein D is the width of the aggregated DRC ribbon.

This area of contact corresponds to a length of DRC nanoscaffold of about \( 8 \times 10^5 \) km/cm². These values explain why the solvated DRC molecule scaffold profoundly impacts the surrounding gel or polymer matrix. Clear evidence of the strong coupling between the gel or polymer matrix and the DRC scaffold is provided by the enhanced orientation of polystyrene chains when a polystyrene fiber is drawn from a polystyrene melt. This is revealed by the formation of two equatorial maxima in the wide-angle X-ray diffraction pattern. In particular, polystyrene and scaffolded polystyrene (i.e., containing 1 weight % DRC molecules) were pressed into plates of 3 mm thickness at 110°C for 20 minutes. Specimens (10 x 5 mm) then were cut from the plates, and the fibers were drawn up to \( \lambda = 2 \) at 120°C. The X-ray samples were cut from the central part of the frozen fibers. The orientation in all tested samples was homogeneous over a multiple length scale of the scattering volume. The diameter of the X-ray beam was 0.5 mm, which is significantly smaller than the characteristic size of the central sample area (about 3 mm).

The reflections correspond in real space to the intermolecular separation of about 9 angstroms between polystyrene chains (see Fig. 5B). This effect is not observed when a fiber is drawn
from molten polystyrene under the same conditions (Fig. 5A). It is, therefore, theorized that the observed birefringence in the scaffolded polystyrene has contributions from both the polystyrene matrix and the small weight percent of self-assembling DRC molecules.

To further demonstrate the nanoscaffold structure provided by the present DRC compounds, binary solvents containing cadmium ions were used as the medium for gel formation. The DRC ribbons are very stable, and, mineralization proceeded without destroying the DRC ribbons. Gels formed from a DRC compound of the present invention, therefore, are an excellent media for templating the growth of one-dimensional nanostructures of a semiconductor material, like cadmium sulfide.

In particular, DRC compound of structural formula (1) (10 mg), cadmium nitrate (20 mg of 0.1M THF solution), and dichloromethane (1 g) were placed in a capped vial, and heated at 70°C until all the solid material was dissolved. The resulting solution was cooled to room temperature, and the gel was aged for 6 hours. The gel then was exposed to a stream of hydrogen sulfide. Diffusion of hydrogen sulfide into the gel was carried out from the top of the vial at room temperature for 1 hour at a flow rate 5 mL/min. The conversion of cadmium nitrate to cadmium sulfide was accompanied by appearance of a green-yellow color. After the reaction was completed, the gel remained transparent and no precipitation was observed. The resulting gel was dissolved in THF, and a green-yellow precipitate was formed within ten minutes. Samples for transmission
electron microscopy (TEM) experiments were prepared by dispersing the precipitated powder in THF, and evaporating a drop of this suspension on a holey carbon-coated copper TEM grid.

If the nanoscaffold contains a hydrophilic section where phenolic groups are localized, cadmium sulfide crystals were expected to nucleate at such hydrophilic sections and grow to a size with at least one dimension comparable to dendron-rod domains. Interactions between rod-dendron domains and metal ions are encouraged by the presence of both phenolic groups and ester bond dipoles. The gels turned a green-yellow color after cadmium sulfide crystals formed, and subsequent analysis by transmission electron microscopy revealed that inorganic ribbons form (gels of ethylhexyl methacrylate). Overall, the above test illustrates an excellent method of mineralizing a polymer utilizing a scaffold comprising a DRC compound of the present invention.

The above discussion focuses on the gelling and polymerization of styrene by a DRC compound of the present invention. However, the addition of a DRC compound to other organic monomers also provides a birefringent gel and a birefringent polymer. Preferred organic monomers contain an aromatic moiety, but other monomers also can be gelled and polymerized.

Accordingly, a present DRC molecule can be added to the following nonlimiting monomers to provide a birefringent gel, and, ultimately, a birefringent polymer: methyl methacrylate, 2-ethylhexyl methacrylate, acrylic acid, methacrylic acid,
acrylonitrile, ethacrylic acid, \( \alpha \)-chloroacrylic acid, \( \alpha \)-cyanoacrylic acid, \( \beta \)-methacrylic acid (crotonic acid), \( \alpha \)-phenylacrylic acid, \( \beta \)-acyroyloxypropionic acid, sorbic acid, \( \alpha \)-chlorosorbic acid, angelic acid, cinnamic acid, p-chlorocinnamic acid, vinyl sulfonic acid, allyl sulfonic acid, vinyl toluene sulfonic acid, styrene sulfonic acid, acrylic and methacrylic sulfonic acids, such as sulfoethyl acrylate, sulfoethyl methacrylate, sulfo-propyl acrylate, sulfopropyl methacrylate, 2-hydroxy-3-methacryloxypropyl sulfonic acid, sulfated hydroxyethyl acrylate, sulfated hydroxypropyl methacrylate, methacryloxy ethyl phosphate, isoprene, an alkene or alkyne containing six to twelve carbon atoms, a halogenated alkene or alkyne containing four to twelve carbon atoms, aziridine, styrene oxide, methyl vinyl ether, styrenic compounds having the formula

\[
\begin{align*}
R^1 \cdot \text{C} &= \text{CH}_2 \\
\end{align*}
\]

wherein \( R^1 \) represents hydrogen or a \( C_{1-4} \) alkyl group, and wherein the phenyl ring is optionally substituted with one to four \( C_{1-4} \) alkyl or hydroxy groups, ethyl (meth)acrylate, isopropyl (meth)acrylate, n-propyl (meth)acrylate, n-butyl (meth)acrylate, \( C_{1-6} \)-alkyl (meth)acrylates including, but are not limited to, isobutyl, pentyl, isoamyl, hexyl, 2-ethylhexyl,
cyclohexyl, decyl, isodecyl, benzyl, lauryl, isobornyl, octyl, and nonyl (meth)acrylates, α-methylstyrene, β-methylstyrene, p-methylstyrene, t-butylstyrene, vinyl benzoate, isopropenyl acetate, a halostyrene, isoprene, vinyl toluene, vinyl naphthalene, methacrylonitrile, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl stearate, isobutoxy-methyl acrylamide, vinyl amine, allyl amine, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 3-hydroxypropyl methacrylate, 2-hydroxypropyl methacrylate, glycidyl acrylate, glycidyl methacrylate, vinyl glycidyl ether, allyl glycidyl ether, and the like, and mixtures thereof. As used herein, halo or halogenated refers to fluoro, chloro, bromo, and iodo.

In addition to the above monomers, monomers that are a gas at 30°C and atmospheric pressure also can be used. Such gaseous monomers include, but are not limited to, C₂-C₅ hydrocarbons and halogenated C₂-C₅ hydrocarbons containing one or more carbon-carbon double bonds and/or triple bonds. Nonlimiting examples of gaseous monomers that can be used with DRC molecules of the present invention to provide birefringent articles of manufacture include, but are not limited to, ethylene, propylene, butene, acetylene, butadiene, ethylene oxide, butadiyne, isopropenyl chloride, vinyl chloride, isobutylene, vinyl bromide, vinylidene fluoride, vinyl fluoride, propyne, butyne, tetrafluoroethylene, and similar alkene, alkynes, and halogenated derivatives thereof, and mixtures thereof.

A birefringent gel containing a DRC compound and an organic monomer typically is polymer-
ized to form a birefringent polymer. Typically, the polymerization is a free radical polymerization performed on the neat birefringent gel, or performed by suspension or emulsion polymerization techniques known to persons skilled in the art.

Polymerization of the birefringent gel can be performed in the presence of a polymerizable crosslinker, conventionally a polyunsaturated organic monomer. Examples of crosslinking polyvinyl monomers include, but are not limited to, polyacrylic (or polymethacrylic) acid esters represented by the following formula (I); and bisacrylamides, represented by the following formula (II).

\[
\begin{align*}
\text{CH}_2=\text{CH} & \quad \text{H}\text{C}=\text{CH}_2 \\
\text{O}=\text{C}-\text{O}-\text{X} & \quad \text{O}-\text{C}=\text{O} \\
& \quad k
\end{align*}
\]

\( \text{(I)} \)

wherein \( X \) is ethylene, propylene, trimethylene, cyclohexyl, hexamethylene, 2-hydroxypropylene, \(-(\text{CH}_2\text{CH}_2\text{O})_p\text{CH}_2\text{CH}_2^-\), or

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
& \quad -(\text{CH}_2-\text{CH}-\text{O})_r\text{CH}_2-\text{CH}-
\end{align*}
\]

\( p \) and \( r \) are each an integer 5 to 40, and \( k \) is 1 or 2;
CH₂=CH

O=C-NH(CH₂CH₂NH)₁C=O

(II)

wherein 1 is 2 or 3.

Specific crosslinking monomers include, but are not limited to, 1,4-butanediol diacrylate, 1,4-butanediol dimethacrylate, 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, ethoxylated bisphenol A diacrylate, ethoxylated bisphenol A dimethacrylate, ethylene glycol dimethacrylate, 1,6-hexanediol diacrylate, 1,6-hexanediol dimethacrylate, neopentyl glycol dimethacrylate, polyethylene glycol diacrylate, polyethylene glycol dimethacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, tripropylene glycol diacrylate, tetraethylene glycol diacrylate, tetraethylene glycol dimethacrylate, dipentaerythritol pentaacrylate, pentaerythritol tetraacrylate, pentaerythritol triacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, tris(2-hydroxyethyl)isocyanurate triacrylate, tris(2-hydroxyethyl)isocyanurate triacrylate, tris(2-hydroxyethyl)isocyanurate trimethacrylate, divinyl esters of a polycarboxylic acid, diallyl esters or a polycarboxylic acid, triallyl terephthalate, diallyl maleate, diallyl fumarate, hexamethylenekismaleimide, trivinyl trimellitate, divinyl adipate, diallyl succinate, a divinyl ether
of ethylene glycol, cyclopentadiene diacrylate, tetraallyl ammonium halides, divinylbenzene, divinyl ether, N,N'-methylenebisacrylamide, N,N'-methylenebismethacrylamide, trimethylolpropane triacrylate, and mixtures thereof.

The crosslinking monomer typically is admixed with the organic monomer prior to gelling the organic monomer with a DRC compound. In addition, a polymerization initiator can be added to the organic monomer prior to gellation to facilitate subsequent polymerization of the gel. The initiator can be a photoinitiator, a thermal initiator, or other type of initiator known to persons skilled in the art, typically in an amount of about 0.1% to about 5%, by weight of the organic monomers.

The DRC compounds of the present invention have the unexpected ability to form birefringent gels when added to an organic medium, like an organic solvent or organic monomer. The birefringent organic monomer gel can be polymerized to form a birefringent polymer. Surprisingly, a melt of the birefringent polymer also is birefringent, and birefringence is maintained even after melting the birefringent polymer several times. It also is envisioned that a birefringent polymer can be obtained by adding a DRC compound of the present invention to a melt of a polymer. A birefringent polymer melt then can be formed into an article of manufacture, for example, by drawing the birefringent melt into a fiber to provide an optical fiber that is macroscopically oriented and capable of transmitting light beams.
Obviously, many modifications and variations of the invention as hereinbefore set forth can be made without departing from the spirit and scope thereof, and, therefore, only such limitations should be imposed as are indicated by the appended claims.
WHAT IS CLAIMED IS:

1. A compound having a general triblock structure

   D-R-C,   D-C-R, or   C-D-R,

wherein block D is a dendritic block, R is a rigid oligomer or polymer, and block C is a flexible oligomer or polymer, and wherein the bonds connecting the D, R, and C blocks are covalent bonds.

2. The compound of claim 1 having the structure

   D-R-C.

3. The compound of claim 1 wherein block C is linear, and has a weight average molecular weight of about 200 to about 10,000.

4. The compound of claim 1 wherein block C is hydrophobic.

5. The compound of claim 4 wherein the hydrophobic block C comprises ethylene, propylene, vinyl methyl ether, a chlorinated vinyl monomer, a fluorinated vinyl monomer, or mixtures thereof.

6. The compound of claim 1 wherein block C is hydrophilic.
7. The compound of claim 6 wherein the hydrophilic block C comprises ethylene oxide, aziridine, or a mixture thereof.

8. The compound of claim 1 wherein block C contains one or more reactive group.

9. The compound of claim 8 wherein the reactive group is selected from the group consisting of carbon-carbon unsaturation, hydroxy, amino, carboxy, and cyano.

10. The compound of claim 1 wherein block C contains one or more nonreactive group.

11. The compound of claim 10 wherein the nonreactive group is selected from the group consisting of methyl, ethyl, isopropyl, halo, and CF₃.

12. The compound of claim 1 wherein block R is linear, and has a weight average molecular weight of about 200 to about 10,000.

13. The compound of claim 1 wherein a ratio of C block monomer units to R block monomer units is about 2:1 to about 4:1.
14. The compound of claim 1 wherein block R comprises one or more of acetylene, a bifunctional phenyl monomer, a biphenyl monomer having a functional group on each phenyl ring, a compound having the structure

![Chemical Structure](image)

wherein A is \((\text{CH}_2)_n\), O, S, or NH, n is 1 or 2, and the Y groups are capable of undergoing a condensation reaction.

15. The compound of claim 14 wherein the Y groups, independently, are selected from the group consisting of \(-\text{CO}_2\text{H}, -\text{COCl}, -\text{CO}_2\text{R}, -\text{OH}, -\text{SH}, -\text{CONH}_2, -\text{CONHR}, -\text{NH}_2, -\text{NHR},\) and \(-\text{OSiR}_3\), wherein R is \(\text{C}_1-\text{C}_4\) alkyl.

16. The compound of claim 1 wherein block D is branched.
17. The compound of claim 16 wherein block D comprises

\[
\begin{array}{c}
\text{Y} \\
\text{CO}_2\text{H} \\
\text{Y}
\end{array}
\]

wherein the Y groups, independently, are selected from the group consisting of -CO₂H, -COCl, -CO₃R, -OH, -SH, -CONH₂, -CONHR, -NH₂, -NHR, and -OSiR₃, wherein R is C₁-C₄ alkyl.
18. The compound of claim 1 having the structure

19. An aggregate comprising molecules of a compound of claim 1.

20. The aggregate of claim 19 in the form of a ribbon.
21. A method of forming an organic gel and imparting order to an organic medium comprising adding about 0.05% to about 2% of a compound of claim 1, by weight of the organic medium, to the organic medium, and forming a birefringent organic gel.

22. The method of claim 21 wherein the organic medium comprises an organic solvent.

23. The method of claim 22 wherein the organic solvent contains an aromatic moiety, a halo moiety, or both.

24. The method of claim 21 wherein the organic medium comprises an organic monomer.

25. The method of claim 24 wherein the organic monomer contains an aromatic moiety.
26. The method of claim 24 wherein the organic monomer is selected from the group consisting of methyl methacrylate, 2-ethylhexyl methacrylate, acrylic acid, methacrylic acid, acrylonitrile, ethacrylic acid, α-chloroacrylic acid, α-cyanoacrylic acid, β-methylacrylic acid (crotonic acid), α-phenylacrylic acid, β-acryloxypropionic acid, sorbic acid, α-chlorosorbic acid, angelic acid, cinnamic acid, p-chlorocinnamic acid, vinyl sulfonic acid, allyl sulfonic acid, vinyl toluene sulfonic acid, styrene sulfonic acid, a (meth)acrylic sulfonic acid, sulfoethyl acrylate, sulfoethyl methacrylate, sulfopropyl acrylate, sulfopropyl methacrylate, 2-hydroxy-3-methacryloyxpropyl sulfonic acid, sulfated hydroxyethyl acrylate, sulfated hydroxypropyl methacrylate, methacryloxy ethyl phosphate, isoprene, an alkene or alkyne containing six to twelve carbon atoms, a halogenated alkene or alkyne containing four to twelve carbon atoms, aziridine, styrene oxide, methyl vinyl ether, a styrene compound having a formula

\[
\begin{align*}
R^1 & \rightleftharpoons CH_2 \\
\end{align*}
\]

wherein \( R^1 \) represents hydrogen or a C\(_{1-4}\) alkyl group, and wherein the phenyl ring is optionally substituted with one to four C\(_{1-4}\) alkyl or hydroxy groups, ethyl (meth)acrylate, isopropyl (meth)acrylate, n-
propyl (meth)acrylate, n-butyl (meth)acrylate, a 
C₄₋₁₆ alkyl (meth)acrylate, α-methylstyrene, β-methyl-
styrene, p-methylstyrene, t-butylstyrene, vinyl 
benzoate, isopropenyl acetate, a halostyrene, iso-
prene, vinyl toluene, vinyl naphthalene, methacrylo-
nitrile, vinyl acetate, vinyl propionate, vinyl 
butyrate, vinyl stearate, isobutoxymethyl acryl-
amide, vinyl amine, allyl amine, 2-hydroxyethyl 
methacrylate, 2-hydroxyethyl acrylate, 3-hydroxy-
propyl methacrylate, 2-hydroxypropyl methacrylate, 
glycidyl acrylate, glycidyl methacrylate, vinyl 
glycidyl ether, allyl glycidyl ether, and mixtures 
thereof.

27. The method of claim 26 wherein the 
organic monomer comprises a styrenic compound having 
the formula

\[
\begin{align*}
\text{R}^1 \text{C} & \equiv \text{CH}_2 \\
\end{align*}
\]

a C₁₋₁₆ alkyl(meth)acrylate, or a mixture thereof.

28. The method of claim 24 wherein the 
organic monomer is a gas.
29. The method of claim 28 wherein the organic monomer is selected from the group consisting of a C$_3$-C$_5$ hydrocarbon containing at least one carbon-carbon double bond or triple bond, a halogenated C$_2$-C$_5$ hydrocarbon containing at least one carbon-carbon double bond or triple bond, ethylene, propylene, butene, acetylene, butadiene, ethylene oxide, butadiyne, isopropenyl chloride, vinyl chloride, isobutylene, vinyl bromide, vinylidene fluoride, vinyl fluoride, propyne, butyne, tetrafluoroethylene, and mixtures thereof.

30. A method of manufacturing a polymer that exhibits liquid crystal-like properties comprising:

(a) admixing an organic monomer and about 0.05% to about 2% of a compound of claim 1, by weight of the organic monomer, to form a birefringent monomer gel; and

(b) subjecting the birefringent monomer gel to polymerization conditions to form a solid birefringent polymer.

31. The method of claim 30 wherein the organic monomer provides an amorphous or semi-crystalline polymer in the absence of a compound of claim 1.

32. The method of claim 30 wherein the birefringent gel is mineralized by incorporating metal ions into the birefringent monomer gel.
33. The method of claim 30 wherein the birefringent monomer gel further comprises a polymerization initiator, a polymerizable crosslinker, or a mixture thereof.

34. A method of inducing liquid crystal-like properties into an amorphous or semi-crystalline polymer comprising adding about 0.05% to about 2%, by weight of the polymer, of a compound of claim 1 to the amorphous or semi-crystalline polymer.

35. A method of manufacturing an article that exhibits liquid crystal-like properties comprising:

(a) admixing an organic monomer and about 0.05% to about 2% of a compound of claim 1, by weight of the organic monomer, to form a birefringent monomer gel;

(b) subjecting the birefringent monomer gel to polymerization conditions to form a solid birefringent polymer;

(c) melting the solid birefringent polymer to form a birefringent polymer melt; and

(d) forming the birefringent polymer melt into a solid, birefringent article.

36. The method of claim 35 wherein the forming step (d) is drawing of a fiber.

37. The method of claim 36 wherein the article is an optical fiber.
38. The method of claim 35 wherein the forming step (d) is a molding step.

39. A method of manufacturing an article that exhibits liquid crystal-like properties comprising:

(a) admixing an organic monomer and about 0.05% to about 2% of a compound of claim 1, by weight of the organic monomer, to form a birefringent monomer gel;

(b) forming the birefringent monomer gel into a shape of the article; and

(c) subjecting the birefringent monomer gel to polymerization conditions to form a solid birefringent article.
FIG. 4
FIG. 7
FIG. 8
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F297/00  C08F297/02  C08G83/00  C08F293/00  C09K19/20
                                    GO2F1/00  C08L53/00

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 7 C08F  C08L  C08G  C09K  GO2F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>WO 98 58970 A (EXXON CHEMICAL PATENTS INC) 30 December 1998 (1998-12-30)</td>
<td>1-5, 10-12, 16,19,20</td>
</tr>
<tr>
<td></td>
<td>* page 4, line 17-21 ; page 3, line 19 – page 4, line 16 ; page 4, line 22-25 ; page 6, line 28 – page 8, line 11 ; page 10, line 7 – page 11, line 31 ; page 4, line 26 – page 5, line 2 ; page 6, line 13-16* page 9, line 2,3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>* claims 1-16 * column 2, line 8 -column 7, line 67</td>
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</table>

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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*s" document member of the same patent family

Date of the actual completion of the international search
5 January 2001

Date of mailing of the international search report
11/01/2001

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Authorized officer
Hammond, A
<table>
<thead>
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<th>Category</th>
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