

POLYMERIZATION OF LOW GRADE DCPD MONOMERS USING AN OLEFIN METATHESIS CATALYST

BACKGROUND

The present invention relates to polydicyclopentadiene (polyDCPD) materials and methods for synthesizing these materials. More particularly, the present invention relates to the use of Ring Opening Metathesis Polymerization (ROMP) reactions for synthesizing polyDCPD.

5 PolyDCPD is an extremely technologically and commercially important polymer material. It is a tough, rigid, thermoset polymer with high modulus, excellent impact strength, and excellent chemical resistance. As a result of these combination of properties, the material finds extensive use in a variety of applications that require toughness and chemical resistance
10 including use in industrial housings, chlorine cell covers, waste water treatment equipment, water vehicles, and snow mobiles.

 Because of the commercial importance of polyDCPD, there has been extensive research into methods for producing this material. One method that has attracted considerable attention is the production of polyDCPD by the
15 ROMP of dicyclopentadiene (DCPD) monomers using a metathesis catalyst system. The polyDCPD produced *via* the ROMP reaction may be post cured to increase the cross-link density of the polyDCPD material. The original catalyst systems used for the ROMP of DCPD were of the Ziegler type. These catalysts were rather ill-defined, and were formed by the reaction of an
20 early transition metal halide with a reducing agent such as an alkyl aluminum halide. A variety of other catalyst systems have also been developed based on tungsten or molybdenum; however, all of the previous catalyst systems have at least two important drawbacks.

 First, the previous catalyst systems are all easily poisoned by
25 impurities and the monomer starting material must therefore be highly purified and water and alcohols must be excluded from the reaction mixture. See for example U.S. Patent No. 4,661,575 which states that "the presence of

water interferes with polymerization of both the catalyst and the activator" and "the water content of the starting material should be below about 100 p.p.m." The monomer starting material used in the conventional processes usually consists of greater than about 99% pure DCPD monomer and this starting material is considerably more expensive than less pure, low grade, monomer. In fact, in the conventional processes the low grade, commercially available monomer must be preprocessed before it may be used as the starting material in the ROMP reaction. U.S. patent No. 4,661,575 states that "the preferred commercially available material [endo-DCPD] normally has a purity of 96-97%," and "the commercially available material should be purified to prevent impurities from inhibiting the polymerization." In addition to the added expense of purchasing and purifying the starting material for use in the conventional processes, a further drawback of having to use highly pure monomer is that the starting material must be stored under stringent conditions to ensure that it is not contaminated. These drawbacks result in increased cost and increased difficulty in handling of the raw materials; considerations which become extremely important in the large-scale production of polyDCPD articles.

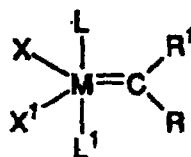
The second drawback of the conventional processes is that not only are the starting materials expensive and difficult to handle but the polyDCPD produced using these processes may possess undesirable physical characteristics. Most importantly, some of the polyDCPD formulations produced using the conventional catalyst systems are blackened or darkened in appearance and are opaque. The black color of these materials increases the difficulty of producing different colored polyDCPD articles by the addition of pigments or dyes to the polymer material. Additionally, since the materials are opaque they cannot be used in applications that require transparent or translucent materials. These undesirable physical characteristics reduce the possible uses of the conventionally produced materials in some industrially and commercially important applications.

For these reasons there exists a need for a method for producing polyDCPD that does not require the use of highly pure DCPD monomer as a starting material. It would further be desirable to produce a polyDCPD material that is transparent or translucent in the absence of additives and that
5 can be produced in a variety of colors by the addition of dyes or pigments while still retaining excellent physical and chemical properties.

SUMMARY

The present invention addresses these needs by providing a method for
10 producing polyDCPD that uses impure DCPD monomers as a starting material. The present invention also provides a polyDCPD material that is transparent or translucent in its natural state and possesses excellent properties such as corrosion resistance and toughness. The polyDCPD material of the present invention can also be produced in a variety of colors by the addition
15 of dyes or pigments.

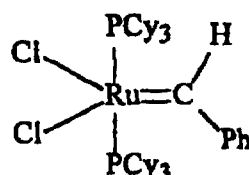
One embodiment of the invention is a method for producing polyDCPD *via* the ROMP of an impure DCPD starting material. In this method a Ruthenium or Osmium carbene complex catalyst is contacted with a DCPD starting material containing less than about 97% by weight of DCPD
20 monomer. The specific Ruthenium or Osmium carbene complex catalysts that may be used include a Ruthenium or Osmium metal center that is in a +2 oxidation state, has an electron count of 16, and is pentacoordinated. These catalysts are stable in the presence of a variety of functional groups including hydroxyl, thiol, ketone, aldehyde, ester, ether, amine, imine, amide, nitro,
25 carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, and halogen; therefore, the DCPD starting material may include impurities containing any of these functional groups. In addition, the DCPD monomers themselves may be functionalized with one or more of the above functional groups without poisoning the catalyst. A preferred version of the Ruthenium
30 or Osmium carbene complex catalysts have the formula



5 where M may be Os or Ru; R and R¹ may be the same or different and may be hydrogen or a substituent group including C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl; X and X¹ may be the same or
 10 different and may be any anionic ligand; and L and L¹ may be the same or different and may be neutral electron donor. The substituent R and R¹ groups may be substituted with one or more groups including C₁-C₃ alkyl, halide, C₁-C₃ alkoxy, and phenyl. The phenyl group may be substituted with one or more groups including halide, C₁-C₃ alkyl and C₁-C₃ alkoxy. In addition to
 15 the above groups, the substituent group may be substituted with one or more functional groups selected from the group consisting of hydroxyl, thiol, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, and halogen.

The preferred catalyst for use in the present invention has the formula

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where Cy is cyclohexyl or cyclopentyl and Ph is phenyl.

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In another embodiment of the invention, the ROMP reaction may be carried out in the presence of a gel modification additive which may be used to control the rate of the ROMP reaction. Suitable gel modification additives include electron donors and lewis bases. The preferred gel modification additive is triphenylphosphine.

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Optionally, the DCPD starting material may contain a cross-linking agent for initiating additional post cure cross-linking reactions. Post cure

cross-linking reactions may be initiated without the presence of a cross-linking agent; however, the additional cross-linking initiated by the cross-linking agent can lead to materials which possess superior chemical resistance properties.

5 Another embodiment of the invention provides a polyDCPD material that is translucent or transparent and may be colored by the incorporation of dyes or pigments. This transparent or translucent material may be produced by the ROMP polymerization of DCPD using the Ruthenium or Osmium carbene catalysts described above. The transparent or translucent polyDCPD
10 material may be produced using the method described above; however, in contrast to the above method which is limited to using a DCPD starting material of less than about 97% by weight of DCPD monomer, the transparent or translucent polyDCPD material may be produced using a DCPD starting material of any purity.

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DETAILED DESCRIPTION

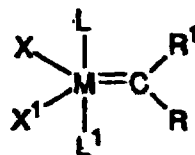
We have found that using certain Ruthenium and Osmium carbene complex catalysts it is possible to catalyze the ROMP reaction of DCPD using an impure DCPD starting material. We have also found that using the
20 Ruthenium and Osmium carbene complex catalysts with both pure and impure DCPD starting materials it is possible to produce a transparent or translucent polyDCPD material. As discussed in the background section, both of these aspects of the invention possess important advantages over the existing methods and materials. In this section, we first describe the
25 Ruthenium and Osmium carbene complex catalysts that may be used in the present invention. In three separate sub-sections, we then describe the general characteristics of the DCPD starting materials, reaction conditions, and polyDCPD materials of the present invention. Finally, we present the results of specific experiments carried out to demonstrate embodiments of the
30 present invention.

Catalysts that may be used in the present invention

The Ruthenium and Osmium carbene complex catalysts that may be used in the present invention and methods of synthesizing these catalysts are taught in this specification and the following references, all of which are incorporated herein by reference: U.S. Patents 5,312,940 and 5,342,909; U.S. patent applications 08/282,827 (filed July 29, 1994), 08/282,826 (filed July 29, 1994), and 08/693,789 (filed July 31, 1996); and U.S. provisional patent application titled "Synthesis of Ruthenium Metathesis Catalysts from Ruthenium Hydride complexes", filed November 15, 1996, inventors Robert H. Grubbs, Tomas Belderrain, and Seth Brown, Attorney Docket No. CTCH-8600.

The Ruthenium and Osmium carbene complex catalysts of the present invention are stable in the presence of a variety of functional groups including hydroxyl, thiol, ketone, aldehyde, ester, ether, amine, amide, nitro acid, carboxylic acid, disulfide, carbonate, carboalkoxy acid, isocyanate, carbodiimide, carboalkoxy, and halogen. Since the catalysts are stable in the presence of these groups, the DCPD starting material impurities, the DCPD monomers themselves, and any substituent groups on the catalyst may include one or more of the above listed groups without deactivating the catalysts.

Generally, the Ruthenium or Osmium carbene complex catalyst that may be used in the present invention include a Ruthenium or Osmium metal center that is in a +2 oxidation state, has an electron count of 16, and is pentacoordinated. These Ruthenium or Osmium carbene complex catalyst may have the formula



where M is Os or Ru

R and R¹ may be the same or different and may be hydrogen or a substituent group which may be C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl. Optionally, the substituent group may be substituted with one or more groups selected from C₁-C₃ alkyl, halide, C₁-C₃ alkoxy, and phenyl. The phenyl group may optionally be substituted with one or more groups selected from halide, C₁-C₃ alkyl, and C₁-C₃ alkoxy. Optionally, the substituent group may be substituted with one or more functional groups selected from hydroxyl, thiol, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, and halogen. In a preferred embodiment, R and R¹ are the same or different and may be hydrogen, substituted aryl, unsubstituted aryl, substituted vinyl, and unsubstituted vinyl; where the substituted aryl and substituted vinyl are each substituted with one or more groups selected from hydroxyl, thiol, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, halogen, C₁-C₃ alkyl, C₁-C₃ alkoxy, unsubstituted phenyl, and phenyl substituted with a halide, C₁-C₃ alkyl or C₁-C₃ alkoxy.

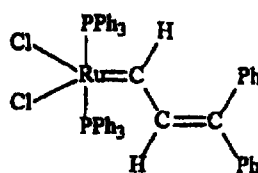
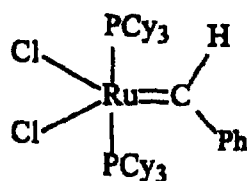
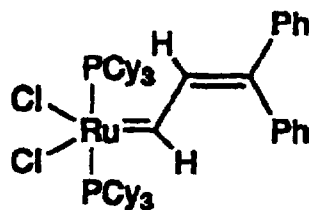
X and X¹ may be the same or different and may generally be any anionic ligand. In a preferred embodiment, X and X¹ are the same or different and may be halogen, hydrogen or a substituent group selected from C₁-C₂₀ alkyl, aryl, C₁-C₂₀ alkoxide, aryloxide, C₃-C₂₀ alkylidicketonate, aryldicketonate, C₁-C₂₀ carboxylate, aryl or C₁-C₂₀ alkylsulfonate, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl, and C₁-C₂₀ alkylsulfinyl. The substituent groups may optionally be substituted with C₁-C₃ alkyl, halogen, C₁-C₃ alkoxy or phenyl. The phenyl may be optionally substituted with halogen, C₁-C₃ alkyl or C₁-C₃ alkoxy. In a more preferred embodiment, X and X¹ are the same or different and may be Cl, Br, I, H or a substituent group selected from benzoate, C₁-C₃ carboxylate, C₁-C₃ alkyl, phenoxy, C₁-C₃ alkoxy, C₁-C₃ alkylthio, aryl, and C₁-C₃ alkyl sulfonate. The substituent groups may be

optionally substituted with C₁-C₃ alkyl or a phenyl group. The phenyl group may optionally be substituted with halogen, C₁-C₃ alkyl or C₁-C₃ alkoxy. In an even more preferred embodiment, X and X¹ are the same or different and are selected from Cl, CF₃CO₂, CH₃CO₂, CFH₂CO₂, (CH₃)₃CO, (CF₃)₂(CH₃)CO, (CF₃)(CH₃)₂CO, PhO, MeO, EtO, tosylate, mesylate, and trifluoromethanesulfonate. In the most preferred embodiment, X and X¹ are both Cl.

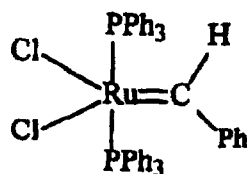
L and L¹ may be the same or different and may generally be any neutral electron donor. In a preferred embodiment, L and L¹ may be the same or different and may be phosphines, sulfonated phosphines, phosphites, phosphinites, phosphonites, arsines, stibines, ethers, amines, amides, sulfoxides, carboxyls, nitrosyls, pyridines, and thioethers. In a more preferred embodiment, L and L¹ are the same or different and are phosphines of the formula PR³R⁴R⁵ where R³ is a secondary alkyl or cycloalkyl and R⁴ and R⁵ are the same or different and are aryl, C₁-C₁₀ primary alkyl, secondary alkyl, or cycloalkyl. In the most preferred embodiment, L and L¹ are the same or different and are -P(cyclohexyl)₃, -P(cyclopentyl)₃, or -P(isopropyl)₃. L and L¹ may also be -P(phenyl)₃.

Preferred catalysts for use in the present invention are ones where M is Ru; R¹ is hydrogen; R is substituted or unsubstituted aryl or substituted or unsubstituted vinyl; X and X¹ are Cl; and L and L¹ are triphenylphosphines or tricycloalkylphosphines such as tricyclopentylphosphine and tricyclohexylphosphine. The substituted aryl and substituted vinyl may each be substituted with one or more groups including C₁-C₃ alkyl, halide, C₁-C₃ alkoxy, and a phenyl group which may be optionally substituted with one or more halide, C₁-C₃ alkyl, or C₁-C₃ alkoxy groups. The substituted aryl and substituted vinyl may also be substituted with one or more functional groups including hydroxyl, thiol, ketone, aldehyde, ester, ether, amine, amide, nitro acid, carboxylic acid, disulfide, carbonate, carboalkoxy acid, isocyanate, carbodiimide, carboalkoxy, and halogen.

Particularly preferred embodiments of the Ruthenium or Osmium carbene complex catalyst include



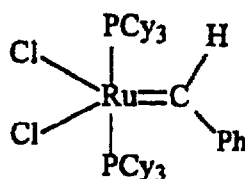
and



25 where Cy is cyclopentyl or cyclohexyl.

The most preferred embodiment of the Ruthenium or Osmium carbene complex catalyst is

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5 where Cy is cyclopentyl or cyclohexyl.

DCPD Starting Materials

The stability of the above Ruthenium and Osmium catalysts to a variety of functional groups allows the present invention to use DCPD starting materials of lower purity than has previously been possible. Specific experiments have shown that the Ruthenium and Osmium carbene complex catalysts described above can catalyze the ROMP of DCPD using starting materials containing as low as about 83% by weight of DCPD monomer. However, due to the stability of the catalysts, the lower limit on the purity of DCPD starting material that may be used is expected to be controlled as much by the desired physical characteristics of the polyDCPD material as by the poisoning of the catalyst. If the DCPD starting material contains too little DCPD monomer the resulting polymer may not have the structural integrity necessary to be useful in the desired applications. Thus the lower limit of the purity of the starting material used in the methods of the invention is a practical limit. Of course, the catalysts may be used with high purity DCPD starting material as well as with low grade, impure DCPD.

The DCPD monomers that may be used in the present invention include both the *endo* and *exo* isomers. In addition, the functional group tolerance of the Ruthenium and Osmium carbene catalysts means that the DCPD monomers may be functionalized to include one or more functional groups. Unless otherwise stated, "DCPD monomer" means either unfunctionalized or functionalized DCPD monomer. The DCPD monomers may be functionalized with a variety of functional groups including hydroxyl, thiol, ketone, aldehyde, ester, ether, amine, amide, nitro acid, carboxylic acid,

disulfide, carbonate, carboalkoxy acid, isocyanate, carbodiimide, carboalkoxy, and halogen.

5 The DCPD starting material may include a variety of impurities including water, alcohols, aromatic or non-aromatic organic species and inorganic species. Specific examples of impurities that may be present include water, alcohols, C5 and C6 cracking fractions, benzene, toluene, cyclopentadiene, and C-9, C-10 and C-11 codimers. Additionally, the DCPD starting material may include trimers and higher oligomers of DCPD. The functional group tolerance of the Ruthenium and Osmium carbene catalysts
10 means that the impurities may include a variety of functional groups including hydroxyl, thiol, ketone, aldehyde, ester, ether, amine, amide, nitro acid, carboxylic acid, disulfide, carbonate, carboalkoxy acid, isocyanate, carbodiimide, carboalkoxy, and halogen.

The DCPD starting material may optionally include one or more gel
15 modification additives which are added to control the pot life of the reaction mixture. The use of gel modification additives is described in detail in utility application filed on December 2, 1996; with application No. 08/759,018; with title "METHOD FOR EXTENDING THE POT LIFE OF AN OLEFIN METATHESIS POLYMERIZATION REACTION"; with Attorney Docket
20 No. APTI-110; and with inventors Charles S. Woodson and Robert H. Grubbs; which is incorporated herein by reference. Generally, the gel modification additive may an electron donor or Lewis base. In a preferred embodiment, the gel modification additive is a neutral electron donor or a neutral Lewis base such as phosphines, sulfonated phosphines, phosphites, phosphinites, phosphonites, arsines, stibines, ethers, amines, amides,
25 sulfoxides, carboxyls, nitrosyls, pyridines, thioethers, nitriles, thiophenes, and furans. The electron donor or Lewis base may optionally contain one or more functional groups selected from the group consisting of hydroxyl, thiol, ketone, aldehyde, ester, ether, amine, amide, nitro acid, carboxylic acid,
30 disulfide, carbonate, carboalkoxy acid, isocyanate, carbodiimide, carboalkoxy, and halogen. In a more preferred embodiment, the gel modification additive

may be triphenylphosphine, tricyclopentylphosphine, tricyclohexylphosphine, triphenylphosphite, pyridine, propylamine, tributylphosphine, benzonitrile, triphenylarsine, anhydrous acetonitrile, thiophene, or furan. The preferred gel modification additives include P(cyclohexyl)₃, P(cyclopentyl)₃, P(isopropyl)₃,
5 P(phenyl)₃, and pyridine. Triphenylphosphine is the most preferred gel modification additive.

The DCPD starting material may optionally include one or more cross-linking agents for initiating additional post cure cross-linking of the polyDCPD. The use of cross-linking agents is described in detail in
10 application No. 08/678,397; filed July 2, 1996; titled "PEROXIDE
CROSSLINKING OF ROMP POLYMERS"; by inventors Robert H. Grubbs and Charles S. Woodson; which is incorporated herein by reference. Preferred cross-linking agents are peroxides, such as alkyl peroxides, particularly *tert*-butyl peroxide or di-*t*-butyl peroxide, 2,5-dimethyl-2,5-di-
15 (*tert*-butylperoxy) hexyne-3, 2,5-dimethyl-2,5-di(*tert*-butylperoxy) hexane or mixtures thereof. The amount of peroxide in the reaction mixture is preferably between 0.01 v% to 10 v% of the total DCPD starting material/catalyst/crosslinking agent mixture.

The DCPD starting material may optionally include additives such as
20 fillers, binders, plasticizers, pigments, dyes etc, as is known in the art. However, because of the functional group tolerance of the catalysts, the range of available additives may be much greater than has been possible using the conventional catalyst systems. Importantly, the DCPD starting material may include pigments and dyes which allow for the production of polyDCPD
25 articles of different colors. As stressed above, this is a great advantage over the previous methods which could not produce colored polyDCPD material. Pigments that have been used to color the polyDCPD material of the present invention include Series 34 pigments manufactured by Ferro Corporation of Cleveland, Ohio. These pigments include a polyether polyol carrier, and
30 specific examples used include 34-58000 (pigment blue 15 a copper phthalocyanine pigment, 50%-75% carrier) 34-88030 (5%-20% carbon black,

>75% carrier), 34-18000 (white, 20%-50% carrier, 50%-75% TiO₂), and 34-48000 (C.I. pigment green 7 a chlorinated copper phthalocyanine pigment, 50%-75% carrier).

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Reaction and Processing Conditions

Generally the ROMP of DCPD is carried out by adding the desired Ruthenium or Osmium carbene complex catalyst to the DCPD starting material which has been heated to a starting resin temperature. Alternatively, the catalyst may be first added to the DCPD starting material and the mixture then heated to the required temperature. The starting resin temperature is not critical; but, as is known, this temperature does affect the rate of the polymerization reaction. The ratio of catalyst to starting material is not critical. Ratios of catalyst to starting material of between about 1:100 and 1:15,000 by weight are preferred. The polyDCPD material produced using catalyst/starting material ratios of greater than about 1:15,000 are soft and rubbery and may therefore not be useful in applications requiring tough rigid materials; such materials may however be useful in other applications requiring different physical properties. The invention may be practiced using catalyst/starting material ratios outside of the above range. The DCPD starting material may optionally be refluxed, filtered, and degassed before the catalyst is added; although, none of these procedures is necessary to practice the invention.

If a gel modification additive, cross-linking agent, or other additive is used it is preferred that the additives be added before the catalyst; although, this is not critical.

Although it is preferred that the reaction be conducted in the absence of a solvent this is not critical. Possible solvents that may be used include organic, protic, or aqueous solvents which are inert under the reaction conditions. Examples of suitable solvents may include aromatic hydrocarbons, chlorinated hydrocarbons, ethers, aliphatic hydrocarbons, alcohols, water, or mixtures thereof.

After polymerization is complete (i.e., after the article has "cured") the polyDCPD article may be post cured to initiate increased cross-linking. As is known, additional cross-linking may be accomplished by post-curing at an elevated temperature. As is well known in the art, other methods may be used to post-cure the polyDCPD material.

Unlike previous catalyst systems, the catalyst/DCPD starting material mixture of the present invention may remain liquid for a considerable period of time depending on the temperature and the amount of gel modification additive present. This characteristic of the present catalyst system allows polyDCPD articles to be made using a variety of polymer processing techniques including molding, open molding, casting, surface coating, filament winding, vacuum impregnation, pouring, RIM, RTM, and others known in the art.

PolyDCPD Material

Unless otherwise stated, "polyDCPD material" means either a post-cured or non-post-cured material; that is, either a material in which the DCPD polymer chains are substantially cross-linked or a material in which the DCPD polymer chains are not substantially cross-linked. In addition, unless otherwise stated, "polyDCPD material" means a polymer produced using either functionalized or unfunctionalized DCPD monomers.

As discussed above, the polyDCPD materials of the present invention possess physical properties which allow them to overcome some of the drawbacks inherent in the previous materials. One of the most visually useful properties of the materials of the present invention is that they can be made transparent or translucent to visible light while retaining excellent chemical and physical properties. These properties allow articles manufactured using the polyDCPD of the present invention to be used in a variety of applications for which the previous, opaque materials could not be used. For example, it is easily possible to read a newspaper article through a 0.5" thick piece of polyDCPD material of the present invention. This example gives a

qualitative measure of the transparency of the polyDCPD according to the present invention. The relatively clear, translucent polyDCPD of the present invention also allows polyDCPD articles to be produced in a variety of colors by the addition of various pigments or dyes.

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Experimental Results

In this section, we present the results of experiments demonstrating the use of low grade DCPD starting materials in the ROMP reactions of the present invention. In sub-sections 2-5, we present the results of experiments using 81%-86% DCPD starting material; then, in sub-section 6, we present the results of experiments using other low grade DCPD starting materials; and, in sub-section 7, we present the results of experiments using low grade DCPD starting materials with gel modification additives.

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1. Synthesis of Ruthenium Complex Catalysts

The specific catalysts used in the experiments below may be synthesized using methods described in the references listed in the *Catalyst* section above.

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2. Composition of 81%-86% Low Grade DCPD Monomer

The % composition by weight of the components of the 81%-86% DCPD monomer used in the experiments in Sections 3 and 5 are as follows:

10	C5's & C6's	0.01
	Benzene	0.01
	Toluene	0
	CPD	0.22
	C-9 Codimers	1.9
15	C-10 Codimers	10.53
	DCPD	82.94
	C-11 Codimers	4.39

20 3. DCPD Polymerization Experimental Procedure

The following are examples of the experimental procedures used in the experiments reported in Section 5.

a. Polymerization Without Reflux Pretreatment of DCPD Monomer.

25 Low grade 81%-86% DCPD (80.86 g, 5000 equiv) was added to a flask containing a stir bar and was heated to a starting resin temperature of about 64°C. $(P(\text{Cyclopentyl})_3)_2\text{Cl}_2\text{RuCHCHPh}_2$ (90 mg, 1 equiv) was then added to the mixture and a slow flow of argon was introduced into the flask. The solution was stirred and at about 2 minute intervals, a small amount of
30 the solution was removed and an Acetone test conducted (See 4, below). When the Acetone test gave a "Flat Ball" result, i.e. some polymerization of

the mixture has started, the solution was poured open to air into a mold that had been previously stored at about 60°C. The time from initial mixing of the monomer and catalyst until pouring is called the "pour time" of the polymerization reaction mixture. In the present example the solution was poured after about 10 minutes. The temperature of the reaction was then monitored and the time and temperature of the peak exotherm temperature recorded. After the reaction was complete, the polyDCPD article was removed from the mold.

b. Polymerization With Reflux Pretreatment of DCPD Monomer.

In this procedure, the low grade 81%-86% DCPD monomer was refluxed prior to the addition of the catalyst. The procedure was as above except that after the DCPD has been added to the flask, and prior to adding the catalyst, the temperature of the DCPD was raised to between about 150°C to about 180°C and the DCPD was refluxed at this temperature for a reflux time. In the results reported here the DCPD monomer was refluxed for about 1 to 8 hours. After refluxing, the DCPD was cooled to the starting resin temperature, the catalyst was added, the Acetone tests carried out, the reaction mixture poured into the mold, the exotherm temperature recorded, and the polyDCPD article subsequently removed from the mold.

c. Polymerization With Peroxide Modifier

In this procedure a peroxide modifier, for initiating additional post cure cross-linking, was added to the low grade 81%-86% DCPD monomer at the same time as the catalyst. An example of this procedure is as follows:

Filtered (with aluminum oxide to remove any inhibitors such as 4-tert-butylcatechol) Low grade 81%-86% DCPD (67.639 g, 5000 equiv) was added to a flask containing a stir bar, and was heated to a starting resin temperature of about 24°C. Tert-Butyl Peroxide (2.005g, 3% v/v), and (P(Cyclopentyl)₃)₂Cl₂RuCHCHPh₂ (75 mg, 1 equiv) were then added to the mixture and a slow flow of argon was introduced into the flask. The solution

was stirred and at about 2 minute intervals, a small amount of the solution was removed and an Acetone test conducted (See 4, below). When the Acetone test gave a "Flat Ball" result, i.e. some polymerization of the mixture has started, the solution was poured open to air into a mold that had been previously stored at about 60°C. The time from initial mixing of the monomer and the catalyst until pouring is called the "pour time" of the polymerization reaction mixture. In the present example the solution was poured after about 10 minutes. The temperature of the reaction was then monitored and the time and temperature of the peak exotherm temperature recorded. After the reaction is complete, the polyDCPD article was removed from the mold.

Optionally, the DCPD monomer may be refluxed prior to the addition of the tert-butyl peroxide and the catalyst.

4. Acetone Test

The Acetone Test is used to measure the extent of the polymerization reaction. In this test, a few drops of the catalyzed DCPD reaction mixture are removed with a small pipet and dropped into a test tube of acetone. Visual inspection yields a qualitative measure of the extent of polymer formation. The visual results are described as "Nothing" (no polymerization), "Cloud", "Flat Ball" (some polymerization), and "Ball."

5. Dependence of Pot life and Peak Exotherm on Reflux Time, Mold Temperature, and Resin Temperature

The experimental procedures described above were carried out for different reflux times, different mold and resin temperatures, and different concentrations of peroxide. For each of the experiments the gel time, i.e. time between mixing and polymerization, and the time to peak exotherm were recorded. These results are summarized in Table 1.

In all cases the catalyst successfully polymerized the low grade 81%-86% DCPD monomer to give polyDCPD.

Table 1

Experiment	T-Butyl Peroxide	Monomer/Catalyst	Reflux Time	Resin Temp [°C]	Mold Temp [°C]	Gel Time (min, approx.)	Peak Exotherm Time [min:sec] Temp [°C]	
A1 ^(a)	No	5000:1	No Reflux	64	60	>30	-	-
A2	No	5000:1	1 hr. 5 min.	60	60	6	6:50	138.1
A3 ^(a)	No	5000:1	1 hr. 5 min.	45	60	>10	-	-
A4	No	5000:1	8 hr.	41	40	3.5	6:29	156.5
A5	No	5000:1	8 hr.	24	61.5	15	16:15	174.5
A6	Yes	5000:1	8 hr.	24	60	>14	16:50	166.1

(a) No peak Exotherm was observed for samples A1 & A3.

6. Experiments B1-B7 using other low grades of DCPD Monomers

The following experiments (#s B1-B7) were carried out to demonstrate that the present invention may be practiced using low grade DCPD monomer starting materials of different purities and with or without gel modification additives.

Experiment #B1

Unfiltered, Refluxed 81-86% DCPD without Gel Modification Additive

Pour into a 250-ml flask with stir bar approximately 87 grams of a Texmark 81-86% DCPD that has been refluxed for 8-hrs. Do not filter. Put the DCPD into a 40.5°C bath to equalize temperature. Add .066g of catalyst $(P(\text{Cyclopentyl})_3)_2\text{Cl}_2\text{RuCHPh}$. Mix for approx. 2-minutes. At this point the acetone test shows a "round ball" degree of polymerization. Pour into a 50°C mold. Peak temperature 149.5°C at 6-minutes and 31-seconds. 264psi HDT was 99.5°C after a 1-hr. post cure at 200°C.

Experiment #B2Unfiltered, unrefluxed 94% DCPD without Gel Modification Additive

- Pour into a 250-ml flask with stir bar approximately 64g of Lyondell 94% DCPD. Do not filter or degass. Add .079g of catalyst $(P(\text{Cyclohexyl})_3)_2$ Cl_2RuCHPh and mix for 3-minutes. Beginning monomer temperature was room temperature. Pour into 45°C. mold. At 43-minutes polymer temperature is approximately the same as the mold temperature, 49.9°C. The sample is very soft to the touch. The mold temperature is increased to 76-78°C. At 63.5-minutes a noticeable exotherm occurs. Peak temperature was 87.1°C @ 63.5-minutes.
- Test stops 95-minutes. The sample is much harder. Sample post cured for 1.25-hr. @ 130°C.

Experiment #B3Unfiltered, unrefluxed 94% DCPD with Gel Modification Additive

- Pour into a 500-ml flask with stir bar approximately 300g of Lyondell 94% DCPD. Do not filter or degass. Add .187g of triphenylphosphine and mix until dissolved. Then add catalyst $(P(\text{Cyclohexyl})_3)_2$ Cl_2RuCHPh .425g and mix. Mold approx. 32°C. and monomer at room temperature. Peak of 47°C. @ 23.5-minutes. After 27.5-minutes added additional mold heat. At 55.5-minutes test concluded with polymer and mold temperature approx. 61°C. After post cure 1-hr. and 10-minutes @ 135°C. sample is very hard with a 264psi HDT of 120.5°C

Experiment #B4Filtered, unrefluxed 94% DCPD with Gel Modification Additive

- Pour into a 250-ml flask with stir bar approx. 64g of Lyondell 94% DCPD that has been filtered and then degassed for about 10-minutes. Add .055g of triphenylphosphine and mix for 5-minutes. Add catalyst $(P(\text{Cyclohexyl})_3)_2$ Cl_2RuCHPh , .054g and mix for 3-minutes. Mold temperature about 38°C. Monomer temperature about 32°C. Gel in about 29-minutes. Left sample in the mold overnight. Next day sample was very firm but possibly slightly soft on top. Post cured for 1.25-hrs. @ 130°C. 264psi was 114°C.

Experiment #B5(Filtered, unrefluxed 94% DCPD without Modification Additive

- Pour into a 250-ml flask with stir bar approx. 300g of Lyondell 94% DCPD. Filter and degass. Add .247g of catalyst $(P(\text{Cyclopentyl})_3)_2 \text{Cl}_2\text{RuCHPh}$ and mix.
- 5 Pour into 33°C mold. Monomer at the beginning of the reaction was room temperature. Had gel at 22-minutes. Peak exotherm was approx. 50°C.(maximum observed).

Experiment #B6

- 10 Filtered, unrefluxed 94% DCPD without Gel Modification Additive

Repeat procedure for example B5 above but raise temperature of the mold to 44.1°C. Peak exotherm observed at 7-minutes and 147.4°C.

Experiment #B7

- 15 Filtered, unrefluxed 94% DCPD without Gel Modification Additive

Repeat procedure for example B6 above but lower mold temperature to 41.5°C. and increase catalyst ratio to 3750:1. Peak at 5-minutes and 35-seconds @ 192°C.

- 20 7. Use of low grades of DCPD Monomers with Gel Modification Additive

We performed the following experiments to demonstrate the use of a gel modification additive with low grade DCPD monomer:

Purification and Degassing of DCPD Monomer

- 25 500 mL DCPD was filtered under vacuum into a one liter round bottom flask through a 150 mL medium porosity sintered glass fritted funnel containing one inch of aluminum oxide. Lower grades of DCPD with lower freezing points can be used after similar purifying treatment.

- 30 To the round bottom flask, containing purified DCPD as above, was added a 1-inch magnetic stir bar. The flask was placed in a water bath 30-35°C and under 0.10 mm Hg vacuum with stirring for from 20 minutes to 1 hour. The degassed

DCPD was then stored under vacuum and protected from light to prevent premature free radical polymerization.

We have found that due to the functional group tolerance of the catalysts of the present invention, we do not need to purify and degass the DCPD monomer
5 before carrying out the polymerization.

DCPD Polymerization Without Gel Modification Additive using
 $P(\text{Cyclopentyl})_3)_2\text{Cl}_2\text{Ru}(=\text{CHCH}=\text{CPh}_2)$ catalyst

To a 250 mL Erlenmeyer flask containing a 1-inch magnetic stir bar, DCPD,
10 purified and degassed, as described above, (147.9 g, 150 mL, 1.12 mol, 5000 eq)
and $P(\text{Cyclopentyl})_3)_2\text{Cl}_2\text{Ru}(=\text{CHCH}=\text{CPh}_2)$ (188.5 mg, 0.224 mmol, 1 eq) were
added. Stirring was initiated and optionally a slow flow of argon was introduced
into the flask. The orange solution was stirred at room temperature for 8 minutes
under argon until it became highly viscous. The solution was then poured open
15 to air into a crystallization dish (14.6 cm in diameter) that had been previously
stored at 120°C. After 2 minutes, the solution began to gel, and the production of
smoke was observed over the following 2 minutes. At this point, the
polymerization appeared complete, and the crystallization dish cooled to room
temperature. The polymer separated from the sides of the crystallization dish
20 easily. The polymer was post-cured at 120°C for 3 hours, resulting in
poly(DCPD) (141.1 g, 95.4% yield).

DCPD Polymerization with Gel Modification Additive using
 $P(\text{Cyclopentyl})_3)_2\text{Cl}_2\text{Ru}(=\text{CHCH}=\text{CPh}_2)$ catalyst.

25 To a flask containing a stir bar, triphenylphosphine (95 mg), and DCPD,
purified and degassed, as described above, (63.991 g) were added. The flask was
stirred under vacuum for about 5 minutes.
 $P(\text{Cyclopentyl})_3)_2\text{Cl}_2\text{Ru}(=\text{CHCH}=\text{CPh}_2)$ (71 mg) was then added to the mixture
and a slow flow of argon was introduced into the flask. The solution was then
30 stirred at room temperature under argon. After 59 minutes, the acetone test (See
below) gave a "Flat Ball" result. The solution was then poured open to air into a

mold that had been previously stored at 60.2°C. The peak temperature of the reaction occurred about 10 minutes after pouring, with a peak temperature of about 158°C.

5 Dependence of pot life on concentration of Gel Modification Additive using
P(Cyclopentyl)₃Cl₂Ru(=CHCH=CPh₂) catalyst: TABLE 2

203 mg of triphenylphosphine was added to 4.052g of 95% DCPD in a test tube and the test tube shaken until the triphenylphosphine was dissolved. 74 mg of (P(Cyclopentyl)₃)₂Cl₂Ru(=CHCH=CPh₂) was then added, shaken by hand and then
 10 mixed with a stir bar for about 1-2 minutes. The mixture was then set aside. After 3 hours 20 minutes, the mixture was still fluid, i.e. only partial polymerization had occurred. The pot life of this reaction mixture is therefore greater than 3 hours 20 minutes. The reaction mixture was added to 60.06g of DCPD. The mixture was stirred slowly under vacuum (this is optional) for a
 15 further 5 minutes and then poured into a mold that had been preheated to 60.8°C. The peak exotherm occurred after about 19 minutes at a temperature of about 69.5°C. The mold was then allowed to cool to room temperature and the polymer removed from the mold and post cured at 190°C for 1 hour.

The experimental procedure described above was carried out for different
 20 concentrations of the gel modification additive and the results are summarized in Table 2.

Table 2

Experiment	Monomer/ Catalyst	PPh ₃ (g)	Catalyst (g)	Pot Life*	Peak Exotherm time (min)
1	5000:1	.203	.074	>3hr 20min	19
2	5000:1	.079	.071	2hr 14 min	~6
3	5000:1	.044	.071	49 min	~4½

"The pot life for Experiments 2 and 3 is the time at which the polymerization mixture is becoming viscous but can still be poured.

DEPENDENCE OF GEL TIME ON CONCENTRATION OF
GEL MODIFICATION ADDITIVE: TABLE 3

USING CATALYST $(P(\text{Cyclohexyl})_3)_2 \text{Cl}_2\text{RuCHPh}$

- 5 The following reactions were carried out using a catalyst of the formula $(P(\text{Cyclohexyl})_3)_2 \text{Cl}_2\text{RuCHPh}$ the results of which are summarized in Table 3. The Experiment numbers relate to the entries in Table 3.

Experiment #4

- 10 Pour into a 250 ml flask with stir bar approximately 64.6g of Velsicol VHP DCPD (about 99% DCPD monomer) that has been filtered and degassed with vacuum. (Note: filtering and degassing are optional). Add .054g of catalyst $(P(\text{Cyclohexyl})_3)_2 \text{Cl}_2\text{RuCHPh}$ and stir for about 3 minutes. Pour into mold. Mold temperature was 34.4°C and the DCPD monomer temperature 31.5°C. Gel
15 time was < 2 minutes & 45 seconds with peak exotherm at 4 minutes & 11 seconds and a peak temperature of 133.8°C.

- 20 Note: Gel time is defined as a) the time at which a stir bar ceases turning in a 250-ml flask during mixing of the catalyst / monomer; or b) the time at which a glass pipet lowered or pushed into a very high viscosity poured sample will no longer pick up or have "cling to" the pipet any of the polymerizing sample.

Experiment #5

- 25 Pour into a 250-ml flask with stir bar approximately 64.0g of Velsicol VHP DCPD that has been filtered and degassed with vacuum. (Note: filtering and degassing are optional). Add .030g of triphenylphosphine and mix for about 5 minutes. Add .054g of catalyst $(P(\text{Cyclohexyl})_3)_2 \text{Cl}_2\text{RuCHPh}$ and stir for about 3 minutes. Pour into mold. Mold temperature was 35.0°C and the DCPD
30 monomer temperature 31.5°C.

Experiment #6

Pour into a 250-ml flask with stir bar approximately 64.0g of Velsicol VHP DCPD that has been filtered and degassed with vacuum. (Note: filtering and degassing are optional). Add .065g of triphenylphosphine and mix for about 5 minutes. Add .054g of catalyst $(P(\text{Cyclohexyl})_3)_2 \text{Cl}_2\text{RuCHPh}$ and stir for about 3 minutes. Pour into mold. Mold temperature was 37.8°C and the DCPD monomer temperature 33°C.

Experiment #7

Pour into a 250-ml flask with stir bar approximately 64.0g of Velsicol VHP DCPD that has been filtered and degassed with vacuum. (Note: filtering and degassing are optional). Add .200g of triphenylphosphine and mix for about 5 minutes. Add .054g of catalyst $(P(\text{Cyclohexyl})_3)_2 \text{Cl}_2\text{RuCHPh}$ and stir for about 3 minutes. Pour into mold. Mold temperature was 36.3°C and the DCPD monomer temperature 31°C.

Experiment #8

In a 25 x 150mm test tube, add approximately 8.132g of Velsicol VHP DCPD that has been filtered and degassed with vacuum. (Note: filtering and degassing are optional). Add .060g of triphenylphosphine and mix until dissolved - about 3-5 minutes. Add .054g of catalyst $(P(\text{Cyclohexyl})_3)_2 \text{Cl}_2\text{RuCHPh}$ and stir for about 3 minutes. Then put test tube into a dry ice / acetone bath for approximately 30 seconds to cool, and then put sample into a 35°F refrigeration and leave overnight.

The following day, weigh out about 56g of Velsicol VHP that has been filtered and degassed with vacuum. (Note: filtering and degassing are optional). Add the frozen Catalyst/TriPhenylPhosphine/DCPD concentrate pellet to the 56g of DCPD monomer and mix until dissolved - about 49 seconds. Resin temperature is 35°C. Mix for 3 minutes longer and pour into a 33.8°C mold. Resin temperature at pour = 35.4°C.

Experiment #9

In a 250-ml flask with stir bar add approximately 64.0g of Lyondell 108 94.04% DCPD that has been filtered and degassed with vacuum. Add .055g of Triphenylphosphine and mix for about 5 minutes. Add .054g of catalyst
5 (P(Cyclohexyl)₃)₂ Cl₂RuCHPh and mix for about 3 minutes. Pour into mold. Mold temperature is 38°C and the DCPD monomer temperature 32°C.

Experiment #10

In a 250-ml flask with stir bar add approximately 64.0g of Lyondell 108 94.04% DCPD that has been filtered and degassed with vacuum. Add .054g of
10 catalyst (P(Cyclohexyl)₃)₂ Cl₂RuCHPh and mix for 3 minutes. Pour into mold. Mold temperature is 38°C and the DCPD monomer temperature 32°C.

Experiment #11

Pour into a 250-ml flask with stir bar approximately 64.1g of Velsicol VHP
15 DCPD that has been filtered and degassed with vacuum. (Note: filtering and degassing is optional). Add .200g of triphenylphosphine and mix for about 5 minutes. Add .080g of catalyst (P(Cyclohexyl)₃)₂ Cl₂RuCHPh and stir for about 3 minutes. Pour into mold. Mold temperature was 32°C and the DCPD monomer temperature 33°C.

20

Experiment #12

In a 25 x 150mm test tube, add approximately 6.0g of Velsicol VHP DCPD that has been filtered and degassed with vacuum. (Note: filtering and degassing are optional). Add .011g of triphenylphosphine and mix until dissolved - about 3-5
25 minutes. Add .054g of catalyst (P(Cyclohexyl)₃)₂ Cl₂RuCHPh and stir for about 3 minutes. Put 58g of Velsicol VHP DCPD into a flask and mix in test tube with Catalyst/Monomer/TriPhenylPhosphine mix for one minute. Pour into mold. Mold temperature is 37.9°C. Resin temperature about 31.8°C.

30

DEPENDENCE OF GEL TIME ON
GEL MODIFICATION ADDITIVE: TABLE 4

5 The following experiments use a similar format to those set forth in Table 3,
but the gel modification additive was varied. The results of these experiments are
summarized in Table 4. These experiments used two different catalysts:
(P(Cyclohexyl)₃)₂ Cl₂RuCHPh and
(PPh₃)₂ Cl₂Ru(=CHCH=CMe₂). Other than for the five specific experiments
described below (Experiment #s 29-33), all results presented in Table 4 are for
10 the (P(Cyclohexyl)₃)₂ Cl₂RuCHPh catalyst. The Experiment numbers relate to the
entries in table 4.

USING CATALYST (P(Cyclohexyl)₃)₂Cl₂RuCHPh: Experiment #s 13-28

15 In a 250-mL flask approximately 64.0g of filtered and degassed Velsicol VHP
DCPD was added. The gel modification additive was added. After mixing until
dissolved or 5 minutes, the catalyst (P(Cyclohexyl)₃)₂ Cl₂RuCHPh was added.
After mixing for about 3 minutes (or less if gelation had occurred) the mixture
was poured into a mold.

20 USING CATALYST (PPh₃)₂ Cl₂Ru(=CHCH=CMe₂): Experiment #s 29-33

The following reactions were carried out using the (PPh₃)₂Cl₂Ru(=CHCH=CMe₂)
catalyst.

Experiment 29

25 Pour into a 250-ml flask with stir bar approximately 64.0g of Velsicol VHP
DCPD that has been filtered and degassed with vacuum. (Note: filtering and
degassing are optional). Add .020g of tricyclohexylphosphine and mix for about
5 minutes. Add .049g of catalyst (PPh₃)₂Cl₂Ru(=CHCH=CMe₂) and mix for 3
minutes. Pour into mold. Mold temperature was 39.2°C and the Resin
30 temperature 33.6°C.

Experiment 30

Pour into a 250-ml flask with stir bar approximately 64.0g of Velsicol VHP DCPD that has been filtered and degassed with vacuum. (Note: filtering and degassing are optional). Add .054g of tricyclohexylphosphine and mix for about 5 minutes. Add .049g of catalyst $(PPh_3)_2Cl_2Ru(=CHCH=CMe_2)$ and mix for 3 minutes. Pour into mold. Mold temperature was 37.5°C and the resin temperature $\approx 32.0^\circ C$.

Experiment #31

Pour into a 250-ml flask with stir bar approximately 64.0g of Velsicol VHP DCPD that has been filtered and degassed with vacuum. (Note: filtering and degassing are optional). Add .032g of tricyclohexylphosphine and mix for about 5 minutes. Add .049g of catalyst $(PPh_3)_2Cl_2Ru(=CHCH=CMe_2)$ and mix for 3 minutes. Pour into mold. Mold temperature was 39.3°C and the resin temperature 32.0°C.

Experiment 32

Pour into a 250-ml flask with stir bar approximately 64.0g of Velsicol VHP DCPD that has been filtered and degassed with vacuum. (Note: filtering and degassing are optional). Add .049g of catalyst $(PPh_3)_2Cl_2Ru(=CHCH=CMe_2)$ and mix for 3 minutes. Pour into mold. Mold temperature was 40.6°C and the Resin temperature 34.0°C.

Experiment #33

In a 25 x 150 mm test tube, add .051g of catalyst $(PPh_3)_2Cl_2Ru(=CHCH=CMe_2)$ and 4-6g of dichloromethane. Add stir bar and mix for about 5 minutes or until catalyst appears to dissolve. Then add .052g tricyclohexylphosphine and purge test tube with argon. Cap test tube and mix at room temperature for 2 hours. After 2 hours, pull off dichloromethane with a vacuum and wash catalyst mixture with another dichloromethane wash. Now add approximately 10.0g of Velsicol VHP DCPD that has not been filtered or degassed, to the test tube and mix

rapidly for about 1 minute or until the catalyst mixture is dissolved in the DCPD. Add the DCPD/catalyst mixture to a flask containing 54.0g of Velsicol VHP DCPD that has not been filtered or degassed. Continue mixing for about 3 minutes total mix time. Pour into mold. Mold temperature was 38.3°C and the
5 resin temperature 32.0°C.

TABLE 3
Triphenylphosphine Level vs. Gel Time

Experiment #	Monomer/ Catalyst	Weight DCPD(g)	PPh ₃ (g)	Catalyst(g)	Mold Temp. °C	Resin Temp. °C	Gel Time (min)	Peak Exotherm Time (min)	Peak Exotherm Temp. °C	Part Cure Schedule	264 psi HDT °C
4	7500:1	64.6	0	.054	34.4	31.5	<2.75	4.18	133.8	a	59
5	7500:1	64.0	.030	.054	35.0	31.5	11.00	16.28	143.6	a	122.5
6	7500:1	64.0	.065	.054	37.8	33.0	25.00	27.00	42.0	a	126.5
7	7500:1	64.0	.200	.054	36.3	31.0	>99.00	53.00	37.6	a	69
8	7500:1	64.0	.060	.054	33.8	35.4	16.00	17.00	38.2	a	130
9	7500:1	64.0	.055	.054	38.0	32.0	>109.00	-	-	a	114
10	7500:1	64g	0	.054	38.0	32.0	<7.00	18.58	68.3	a	109
11	5000:1	64.1g	.200	.080	32.0	33.0	>154.00	-	-	a	128
12	7500:1	64.0	.011	.054	37.9	31.8	<4.00	9.56	161.1	-	-

Cure Schedule

a: 1 hour and 15 minutes @ 130°C

TABLE 4									
Gel Modification Additives vs. Gel Time									
Experiment #	Weight of Catalyst(g)	Weight of DCPD(g)	Gel* Modification Additive	Additive Amount	Mold Temp °C	Resin Temp. °C	Gel Time (min)	Peak Exotherm	
								Time (min)	Temp. °C
13	.054	64.0	#1	.010g	36.4	31.0	6.00	7.33	160.3
14	.054	64.0	#1	.028g	36.2	31.0	9.00	10.83	173.2
15	.054	64.0	#1	.073g	36.3	31.0	21.00	38.30	91.5
16	.054	64.1	#2	.069g	38.6	33.3	6.00	7.20	190.4
17	.054	64.0	#2	.150g	36.3	33.2	11.00	13.75	184.9
18	.054	64.0	#3	.084g	35.9	32.5	none	none	none
19	.054	64.0	#4	.061g	37.1	31.0	10.00	15.10	145.1
20	.054	64.0	#5	.046g	36.6	32.0	none	none	none
21	.054	64.6	#6	.062g	35.0	31.0	none	none	none
22	.056	64.0	#7	.066g	33.1	32.0	1.50	too fast to measure	
23	.054	64.0	#7	.150g	33.0	32.0	≈2.50	4.03	148.4
24	.054	64.3	#8	.062g	34.0	32.0	1.50	too fast to measure	
25	.054	64.0	#8	.290g	≈35.0	32.0	2.75	-	-
26	.054	64.0	#9	.150ml	35.6	32.0	1.23	too fast to measure	
27	.054	64.0	#10	.150ml	33.9	32.0	1.88	too fast to measure	
28	.054	64.0	#11	.150ml	33.6	32.0	1.32	too fast to measure	

29	.049	64.0	#2	.020g	39.2	33.6	9.00	15.00	44.2
30	.049	64.0	#2	.054g	37.5	32.0	12.00	21.00	48.00
31	.049	64.0	#1	.032g	39.3	32.0	>16.00	14.00	14.00
32	.049	64.0	none	none	40.6	34.0	>60.0	-	-
33	.051	64.0	#2	.052g	38.3	32.0	13.00	20.75	111.7

Gel Modification Additives

*#1	Tricyclopentylphosphine	*#2	Tricyclohexylphosphine
*#3	Triphenylphosphite	*#4	Pyridine
*#5	Propylamine	*#6	Tributylphosphine
*#7	Benzonitrile	*#8	Triphenylarsine
*#9	Anhydrous Acetonitrile	*#10	Thiophene
*#11	Furan		



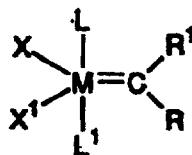
CLAIMS

What is claimed is:

1. A method for making a polyDCPD material *via* the ROMP of a DCPD starting material, the method comprising the step of

- 5 (a) contacting a DCPD starting material that contains less than about 97% by weight of functionalized or unfunctionalized DCPD monomer with a Ruthenium or Osmium carbene complex catalyst that includes a Ruthenium or Osmium metal center that is in a +2 oxidation state, has an electron count of 16, and is pentacoordinated to form a polyDCPD material.

10 2. The method according to claim 1, wherein the Ruthenium or Osmium carbene complex catalyst has the formula



15

where:

M is selected from the group consisting of Os and Ru;

20 R and R¹ are independently selected from the group consisting of hydrogen and a substituent group selected from the group consisting of C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl;

25 X and X¹ are independently selected from any anionic ligand; and

L and L¹ are independently selected from any neutral electron donor.



3. The method according to claim 2, wherein the substituent group is substituted with one or more groups selected from the group consisting of C₁-C₃ alkyl, halide, C₁-C₃ alkoxy, and phenyl.
- 5 4. The method according to claim 3, wherein the phenyl group is substituted with one or more groups selected from the group consisting of halide, C₁-C₃ alkyl, and C₁-C₃ alkoxy.
- 10 5. The method according to claim 2, wherein the substituent group is substituted with one or more functional groups selected from the group consisting of hydroxyl, thiol, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, and halogen.
- 15 6. The method according to claim 2, wherein R and R¹ are independently selected from the group consisting of hydrogen, substituted aryl, unsubstituted aryl, substituted vinyl, and unsubstituted vinyl; and
 wherein the substituted aryl and substituted vinyl are each substituted with one or more groups selected from the group consisting of hydroxyl, thiol,
20 ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, halogen, C₁-C₃ alkyl, C₁-C₃ alkoxy, unsubstituted phenyl, and phenyl substituted with a halide, C₁-C₃ alkyl or C₁-C₃ alkoxy.
- 25 7. The method according to claim 2, wherein L and L¹ are independently selected from the group consisting of phosphine, sulfonated phosphine, phosphite, phosphinite, phosphonite, arsine, stibine, ether, amine, amide, sulfoxide, carboxyl, nitrosyl, pyridine, and thioether.



8. The method according to claim 7, wherein L and L¹ are phosphines independently selected from PR³R⁴R⁵ wherein R³ is selected from the group consisting of secondary alkyl and cycloalkyl and wherein R⁴ and R⁵ are independently selected from the group consisting of aryl, C₁-C₁₀ primary alkyl, secondary alkyl, and cycloalkyl.
9. The method according to claim 8, wherein L and L¹ are independently selected from the group consisting of -P(cyclohexyl)₃, -P(cyclopentyl)₃, and -P(isopropyl)₃.
10. The method according to claim 7, wherein L and L¹ are both -P(phenyl)₃.
11. The method according to claim 7, wherein L and L¹ are the same.
12. The method according to claim 2, wherein X and X¹ are independently selected from the group consisting of halogen, hydrogen; C₁-C₂₀ alkyl, aryl, C₁-C₂₀ alkoxide, aryloxy, C₃-C₂₀ alkyldiketonate, aryldiketonate, C₁-C₂₀ carboxylate, aryl or C₁-C₂₀ alkylsulfonate, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl, or C₁-C₂₀ alkylsulfinyl; each optionally substituted with C₁-C₅ alkyl, halogen, C₁-C₅ alkoxy or with a phenyl group optionally substituted with halogen, C₁-C₅ alkyl or C₁-C₅ alkoxy;
13. The method according to claim 12, wherein X and X¹ are independently selected from Cl, Br, I, H; benzoate, C₁-C₅ carboxylate, C₁-C₅ alkyl, phenoxy, C₁-C₅ alkoxy, C₁-C₅ alkylthio, aryl, or C₁-C₅ alkyl sulfonate; each optionally substituted with C₁-C₅ alkyl or a phenyl group optionally substituted with halogen, C₁-C₅ alkyl or C₁-C₅ alkoxy.



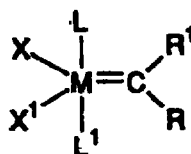
14. The method according to claim 13, wherein X and X¹ are independently selected from the group consisting of Cl, CF₃CO₂, CH₃CO₂, CFH₂CO₂, (CH₃)₃CO, (CF₃)₂(CH₃)CO, (CF₃)(CH₃)₂CO, PhO, MeO, EtO, tosylate, mesylate, and trifluoromethanesulfonate.

5

15. The method according to claim 14, wherein X and X¹ are both Cl.

16. The method according to claim 1, wherein the Ruthenium or Osmium carbene complex catalyst has the formula

10



where:

15

M is Ru;

R¹ is hydrogen;

R is substituted aryl, unsubstituted aryl, substituted vinyl, or unsubstituted vinyl;

X and X¹ are Cl; and

20

L and L¹ are triphenylphosphines or tricycloalkylphosphines.

17. The method according to claim 16, wherein the substituted aryl is substituted with one or more groups selected from the group consisting of C₁-C₅ alkyl, halide, C₁-C₅ alkoxy, unsubstituted phenyl, and phenyl substituted with a halide, C₁-C₅ alkyl or C₁-C₅ alkoxy.

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18. The method according to claim 16, wherein the substituted vinyl is substituted with one or more groups selected from the group consisting of C₁-C₅

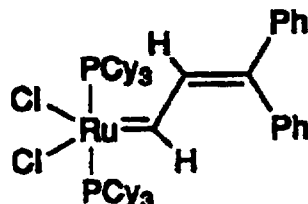


alkyl, halide, C₁-C₃ alkoxy, unsubstituted phenyl, and phenyl substituted with a halide, C₁-C₃ alkyl or C₁-C₃ alkoxy.

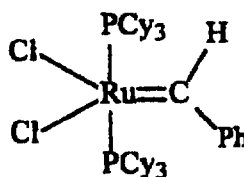
19. The method according to claim 16, wherein the substituted aryl is substituted with one or more functional groups selected from the group consisting of hydroxyl, thiol, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, and halogen.

20. The method according to claim 16, wherein the substituted vinyl is substituted with one or more functional groups selected from the group consisting of hydroxyl, thiol, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, and halogen.

21. The method according to claim 1, wherein the catalyst is selected from the group consisting of



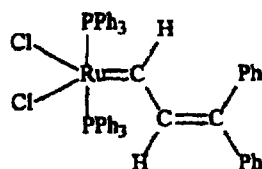
and



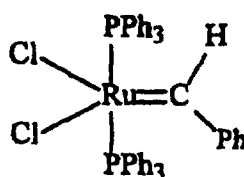
wherein Cy is cyclohexyl or cyclopentyl.



22. The method according to claim 1, wherein the catalyst is selected from the group consisting of



and



23. The method according to claim 1, wherein the DCPD starting material is contacted with the Ruthenium or Osmium carbene complex catalyst in the presence of an electron donor or Lewis base.

24. The method according to claim 23, wherein the electron donor or Lewis base is selected from the group consisting of phosphines, sulfonated phosphines, phosphites, phosphinites, phosphonites, arsines, stibines, ethers, amines, amides, sulfoxides, carboxyls, nitrosyls, pyridines, thioethers, nitriles, thiophenes, and furans.

25. The method according to claim 24, wherein the electron donor or Lewis base is a trialkyl or triaryl phosphine.

26. The method according to claim 23, wherein the electron donor or Lewis base is selected from the group consisting of P(cyclohexyl)₃, P(cyclopentyl)₃, P(isopropyl)₃, and pyridine.



27. The method according to claim 23, wherein the electron donor or Lewis base is $\text{P}(\text{phenyl})_3$.
- 5 28. The method according to claim 23, wherein the electron donor or Lewis base is selected from the group consisting of tricyclopentylphosphine, tricyclohexylphosphine, triphenylphosphite, pyridine, propylamine, tributylphosphine, benzonitrile, triphenylarsine, anhydrous acetonitrile, thiophene, and furan.
- 10 29. The method according to claim 23, wherein the electron donor or Lewis base contains one or more functional groups selected from the group consisting of hydroxyl, thiol, ketone, aldehyde, ester, ether, amine, amide, nitro acid, carboxylic acid, disulfide, carbonate, carboalkoxy acid, isocyanate, carbodiimide, carboalkoxy, and halogen.
- 15 30. The method according to claim 1, wherein the DCPD monomer is a functionalized DCPD monomer that contains one or more functional groups selected from the group consisting of hydroxyl, thiol, ketone, aldehyde, ester, ether, amine, amide, nitro acid, carboxylic acid, disulfide, carbonate, carboalkoxy acid, isocyanate, carbodiimide, carboalkoxy, and halogen.
- 20 31. The method according to claim 1, wherein the DCPD starting material contains about 94% by weight of functionalized or unfunctionalized DCPD monomer.
- 25 32. The method according to claim 1, wherein the DCPD starting material contains between about 81% by weight and about 86% by weight of functionalized or unfunctionalized DCPD monomer.



33. The method according to claim 1, wherein the DCPD starting material includes a cross-linking agent.

5 34. A method according to claim 33, wherein the cross-linking agent comprises a peroxide selected from the group consisting of *t*-butyl peroxide, 2,5-dimethyl-2,5-di-(*tert*-butylperoxy) hexyne-3, di-*tert*-butyl peroxide, and 2,5-dimethyl-2,5-di-(*tert*-butylperoxy) hexane or mixtures thereof.

10 35. A method according to claim 1, wherein the amount of cross-linking agent is between about 0.01 v% and about 10 v% of the mixture of catalyst, cross-linking agent and DCPD starting material.

15 36. The method of claim 33, further comprising the steps of
(b) decomposing the cross-linking agent to form reactive species of the cross-linking agent; and
(c) using said reactive species to form cross-links in the polyDCPD material.

20 37. The method of claim 1, wherein the DCPD starting material is refluxed prior to being contacted with the Ruthenium or Osmium carbene complex catalyst.

25 38. A polymeric material comprising polyDCPD made by the method described in claim 1.

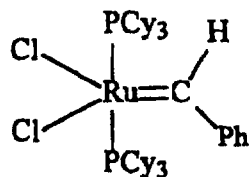
39. The polymeric material according to claim 38, wherein the polymeric material is transparent or translucent.



40. The polymeric material according to claim 37, further comprising a color pigment or color dye.
- 5 41. The polymeric material according to claim 40, wherein the color pigment or color dye includes a polyether polyol.
42. A transparent or translucent polymeric material comprising polyDCPD.
- 10 43. The composition according to claim 42, wherein the polymeric material contains less than about 97% by weight of polyDCPD.
44. The composition according to claim 42, wherein the polymeric material contains more than about 81% by weight of polyDCPD.
- 15 45. The composition according to claim 42, wherein the polyDCPD is cross-linked polyDCPD.
46. The composition according to claim 42, wherein the polyDCPD contains one or more functional groups selected from the group consisting of hydroxyl, 20 thiol, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, and halogen.
- 25 47. A method for making polyDCPD *via* the ROMP of a DCPD starting material, the method comprising the step of contacting a DCPD starting material that contains less than about 97% by weight of DCPD monomer with a Ruthenium or Osmium carbene complex catalyst of the formula



wherein Cy is cyclohexyl
or cyclopentyl.



- 5 48. The method according to claim 47, wherein the DCPD starting material is contacted with the Ruthenium or Osmium carbene complex catalyst in the presence of triphenylphosphine.
- 10 49. The method according to claim 47, wherein the DCPD starting material contains more than about 81% by weight of DCPD monomer.
- 15 50. The method according to claim 47, wherein the DCPD starting material is contacted with the Ruthenium or Osmium carbene complex catalyst in the presence of a cross-linking agent comprising a peroxide selected from the group consisting of *t*-butyl peroxide, 2,5-dimethyl-2,5-di-(*tert*-butylperoxy) hexyne-3, di-*tert*-butyl peroxide, and 2,5-dimethyl-2,5-di-(*tert*-butylperoxy) hexane or mixtures thereof.

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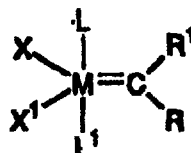
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(54) Title: POLYMERIZATION OF LOW GRADE DCPD MONOMERS USING AN OLEFIN METATHESIS CATALYST

(57) Abstract

Methods for synthesizing polyDCPD via ROMP of low grade DCPD starting materials using Ruthenium or Osmium carbene complex catalyst. Transparent or translucent polyDCPD materials. The Ruthenium or Osmium carbene complex catalysts having



(I)

formula (I), where M may be Os or Ru; R and R¹ may be the same or different and may be hydrogen or substituent group including C₂-C₂₀ alkenyl, C₂-C₂₀ alkynyl, C₁-C₂₀ alkyl, aryl, C₁-C₂₀ carboxylate, C₁-C₂₀ alkoxy, C₂-C₂₀ alkenyloxy, C₂-C₂₀ alkynyloxy, aryloxy, C₂-C₂₀ alkoxycarbonyl, C₁-C₂₀ alkylthio, C₁-C₂₀ alkylsulfonyl and C₁-C₂₀ alkylsulfinyl; X and X¹ may be the same or different and may be any anionic ligand; and L and L¹ may be the same or different and may be neutral electron donor. The low grade DCPD starting materials containing less than about 97 % by weight of DCPD monomers.