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(54) Title: FUNCTIONALISED CARBON NANOTUBES AND METHODS OF PREPARATION

(57) Abstract: The preparation of dithioester functionalised carbon nanotubes (DTE-CNTs) is described. The DTE-CNTs are pre-
pared by reacting suitably functionalised carbon nanotubes with a modified Grignard reagent. The DTE-CNTs are particularly useful
as chain transfer agents in reversible addition fragmentation chain transfer (RAFT) polymerisation reactions, and polymer compos-
ites prepared using the DTE-CNTs are also described.

FUNCTIONALISED CARBON NANOTUBES AND METHODS OF PREPARATION

TECHNICAL FIELD

The present invention relates to functionalised carbon nanotubes and a method for their preparation. More particularly, but not exclusively, it relates to dithioester functionalised carbon

5   nanotubes and their preparation.

BACKGROUND ART

In polymer or copolymer synthesis, achieving a product with a desired molecular weight and a narrow weight distribution, or polydispersity, requires a controlled process. Polymers with a narrow molecular weight distribution can exhibit substantially different behaviour and properties

10   from polymers prepared by conventional means. Living polymerisations provide the maximum degree of control for the synthesis of polymers with predictable, well-defined structures. The characteristics of a living polymerisation include: polymerisation proceeding until all monomer is consumed; number average molecular weight as a linear function of conversion; molecular weight control by the stoichiometry of the reaction; and block copolymer preparation by

15   sequential monomer addition.

Scheme 1

$$I^* \text{ (initiator)} \quad + \quad \text{Monomer} \quad \longrightarrow \quad P_n{}^*$$
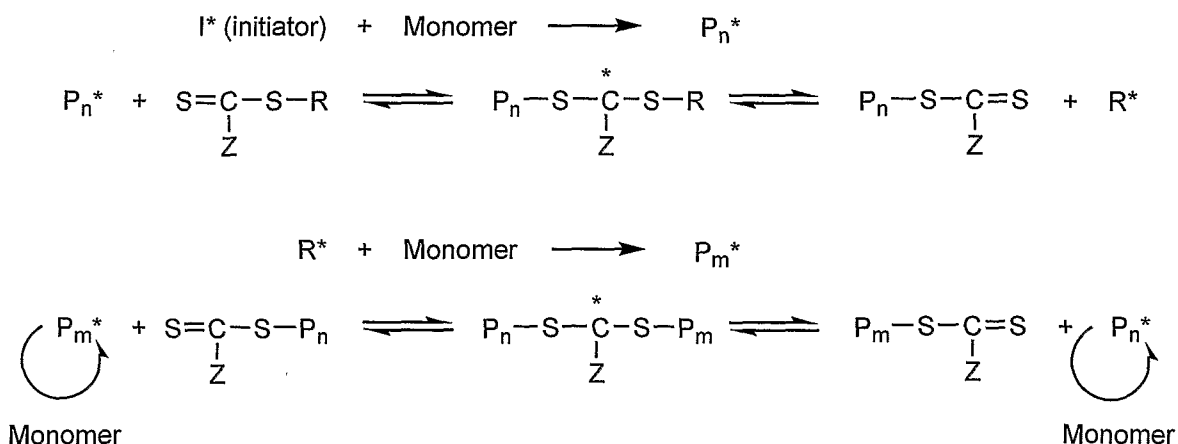
The reversible addition-fragmentation chain transfer (RAFT) process is a free radical polymerisation technique with living polymerisation characteristics. It requires charge transfer

20   agents, typically a carbonylthio compound, or "dithioester". This is introduced at the beginning of the reaction with the monomer. Control in such a RAFT process is thought to be achieved through a degenerative chain transfer mechanism in which a propagating radical reacts with the

dithioester compound to produce an intermediate radical species. This process decreases the number of free radicals available for termination reactions that require two free radicals.

The mechanism of a typical RAFT polymerisation is shown in Scheme 1 above, wherein * denotes a radical.

5   Owing to new developments in the field of free-radical polymerisation, these dithioesters are becoming increasingly important.

Dithioester compounds also have other possible applications, for example as efficient reagents for the modification of peripheral amino acid residues of proteins. Thioacylation is a new way for protein chemical modification. Carboxylic dithio-esters and -acids react selectively and

10   rapidly at room temperature with aliphatic amines such as lysine ε-amino groups leading to thioamide formation, without any other reagent or catalyst.

Therefore, it would be useful to find alternative routes to dithioester preparation.

Carbon nanotubes (CNTs) are long thin cylinders of graphene sheets which have unique electronic, mechanical and thermal properties for their size and shape. Much of this is dependent

15   on the type and chirality of the nanotubes. Carbon nanotubes can be single-walled (SWCNT), multi-walled (MWCNT) or double-walled (DWCNT), all of which may be doped or undoped. Doping may be n- or p-doping.

SWCNTs consist of one graphene sheet rolled into a cylinder, and are normally capped by a half fullerene. SWCNTs typically have diameters of about 1.0-1.8 nm. Depending upon the

20   fabrication technique, SWCNTs are usually produced as mixtures of conductive and semi-conductive tubes. The characteristics of these nanotubes are directly related to their chirality, which gives rise to their unique properties.

MWCNTs typically have 7-20 concentric alternating conductive/semi-conductive graphene cylinders, resulting in tubes which have diameters of about 20-80 nm. MWCNTs are more

25   amenable to functionalisation simply because the number of sheets allows for extensive functionalisation without damaging the inherent properties of the innermost tubes.

DWCNTs have a coaxial structure, containing two concentric graphene cylinders, which alternate from conductive to semi-conductive according to chirality. Like MWCNTs, the outer

tube of the DWCNTs may be functionalised while still retaining the intrinsic properties of the inner tube, which is either semi-conductive or conductive. DWCNTs are generally produced by catalytic chemical vapour deposition.

Numerous attempts have been made to incorporate CNTs into polymers to exploit the
5   exceptional strength and conductive properties of the CNTs. The fundamental control over composite morphologies and interfacial chemical interactions is critical for dramatically enhancing their performance in electronic applications. Although covalent attachment of polymers to CNTs has been achieved, high loadings with poor dispersion of the CNTs dominate composite formation and device fabrication.

10   Ion-conducting polymers, or polymers containing conductive fillers such as carbon black (5-30% by weight loading), are typically employed for electronic applications. However, they suffer from several drawbacks including: having high dopant or filler loadings; being brittle; and being opaque as thin films. CNTs offer a viable alternative.

CNTs are inert but can be chemically functionalised. Functionalisation and derivatisation
15   increases the interfacial binding in composites, providing a mechanism for connecting CNTs together and/or connecting CNTs to substrates. Because of the limited scope of direct covalent sidewall functionalisation at defect sites, traditional chemical treatments such as wet oxidation in concentrated HNO_3/H_2SO_4 are used to functionalise the surface of CNTs with hydroxyl (-OH), carboxyl (-COOH) and carbonyl (>C=O) groups. In the art, carboxyl groups have been
20   converted to the corresponding acid chloride using thionyl chloride, with subsequent amide linkage of an aminoalkanethiol to single-walled nanotubes (SWNTs). SWNTs have also been derivatised by thionyl chloride to produce thiols on the ends of SWNTs — see L. K. Lim *et al.*, *Synthetic Met.* 2003, **139**, 521.

Any discussion of documents, acts, materials, devices, articles or the like which has been
25   included in the present specification is solely for the purpose of providing a context for the present invention. It is not to be taken as an admission that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the present invention as it existed before the priority date.

It is an object of the present invention to: provide an alternative route to dithioester production; and/or provide a mechanism by which a carbon nanotube may be covalently incorporated into a polymer; and/or at least provide the public with a useful choice.

Other objects of the invention may become apparent from the following description which is

5 given by way of example only.

SUMMARY OF THE INVENTION

In a first aspect, the present invention provides a dithioester carbon nanotube (DTE-CNT) of formula (I):

$$Z\text{-}C(OH)(S\text{-}C(=S)R^1)(S\text{-}C(=S)R^2) \quad (I)$$
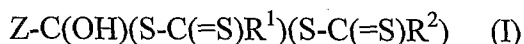
10 wherein Z is a carbon nanotube, and R^1 and R^2 are independently alkyl, alkenyl or aryl, wherein any alkyl, alkenyl or aryl may be optionally substituted.

In one embodiment, R^1 and R^2 are both alkyl. In another embodiment, R^1 and R^2 are both aryl.

Preferably, the DTE-CNT of the invention is water-soluble.

In a further aspect, the present invention provides a method of preparing a DTE-CNT comprising

15 the steps of:

-     functionalising a CNT with a moiety that is susceptible to a Grignard reagent or a modified
      Grignard reagent to provide a functionalised CNT; and
-     reacting the functionalised CNT with a dithiocarboxylated Grignard reagent (DTG) of
      formula (II):

20 $$RC(=S)SMX \quad (II)$$

wherein R is alkyl, alkenyl or aryl, wherein any alkyl, alkenyl or aryl may be optionally substituted; M is Be, Mg, Ca, Sr or Ba; and X is Cl, Br or I;

to obtain one or more DTE-CNTs.

In one embodiment, R is alkyl. In another embodiment, R is aryl.

25 Preferably, M is magnesium.

Preferably, the moiety that is susceptible to a Grignard reagent or a modified Grignard reagent is selected from the group consisting of: acyl halides; alkyl halides; aryl halides; alkyl alcohols; aryl alcohols; ketones; aldehydes; anhydrides; alkyl esters; and aryl esters. More preferably, the

moiety is selected from the group consisting of: acyl halides; anhydrides; alkyl esters; and aryl esters. In a particularly preferred embodiment, the moiety is an acyl halide.

In some embodiments, the step of functionalising the CNT includes the preliminary step of oxidising the CNT. In one embodiment, the CNT is oxidised by chemical treatment, preferably

5   with an acid or a mixture of acids.

The DTG is typically prepared by reacting a Grignard reagent of formula RMX with an aliphatic disulfide of formula $R'S_2$, wherein R' is alkyl, or with carbon disulfide.

A preferred DTG is dithiopropanoic magnesium chloride, $CH_3CH_2C(=S)SMgCl$. Dithiopropanoic magnesium chloride may be prepared by reacting ethylmagnesium chloride,

10   CH_3CH_2MgCl, with CS_2.

The present invention also provides a DTE-CNT prepared substantially according to the method of the invention. Preferably, the DTE-CNT is water-soluble.

In another aspect, the present invention provides use of a DTE-CNT of the invention as a chain transfer agent in a reversible addition fragmentation chain transfer (RAFT) polymerisation.

15   In another aspect, the present invention provides a charge transfer agent, suitable for use in a RAFT polymerisation process, comprising a DTE-CNT of formula (I):

$$Z-C(OH)(S-C(=S)R^1)(S-C(=S)R^2) \quad (I)$$

wherein Z is a carbon nanotube, and R^1 and R^2 are independently alkyl, alkenyl or aryl, wherein any alkyl, alkenyl or aryl may be optionally substituted.

20   In a preferred embodiment, charge transfer agent is water-soluble.

In another aspect, the present invention provides a method of preparing a polymer-CNT composite comprising the steps of:

-      providing a charge transfer agent comprising a DTE-CNT of formula (I):

$$Z-C(OH)(S-C(=S)R^1)(S-C(=S)R^2) \quad (I)$$

25   wherein Z is a carbon nanotube, and R^1 and R^2 are independently alkyl, alkenyl or aryl, wherein any alkyl, alkenyl or aryl may be optionally substituted; and

-      reacting a monomer with the charge transfer agent in a RAFT polymerisation; to provide the polymer-CNT composite.

The monomer is typically a polar monomer that is capable of undergoing a free radical polymerisation process. For example, the monomer may be an acrylate. In one embodiment, the monomer is methylmethacrylate. In another embodiment, the polymer is 2-hydroxyethylmethacrylate. In these embodiments, the monomer may be polymerised in a

5   RAFT polymerisation process under ultraviolet (UV) light.

In one embodiment, the method further comprises applying an external electric field during the RAFT polymerisation to align the CNTs.

Preferably, the DTE-CNT charge transfer agent is water-soluble.

The present invention also provides a polymer-CNT composite prepared substantially according

10   to the method of the invention.

In another aspect, the present invention provides a polymer-CNT composite wherein the CNT is, or is derived from, a DTE-CNT of formula (I):

$$Z\text{-}C(OH)(S\text{-}C(=S)R^1)(S\text{-}C(=S)R^2) \quad (I)$$

wherein Z is a carbon nanotube, and R^1 and R^2 independently alkyl, alkenyl or aryl,

15   wherein any alkyl, alkenyl or aryl may be optionally substituted.

In one embodiment, the CNTs are substantially aligned in the polymer-CNT composite of the invention.

In one embodiment, the polymer-CNT composite of the invention is conductive.

Other aspects of the invention may become apparent from the following description which is

20   given by way of example only and with reference to the accompanying drawings.

As used herein the term "and/or" means "and" or "or", or both.

The term "comprising", or variations such as "comprises", as used in this specification and claims means "consisting at least in part of". That is to say when interpreting statements in this specification and claims which include that term, the features prefaced by that term in each

25   statement all need to be present but other features can also be present.

This invention may also be said broadly to consist in the parts, elements and features referred to or indicated in the specification of the application, individually or collectively, and any or all

combinations of any two or more of said parts, elements or features, and where specific integers are mentioned herein which have known equivalents in the art to which this invention relates, such known equivalents are deemed to be incorporated herein as if individually set forth.

BRIEF DESCRIPTION OF DRAWINGS

5   The invention will now be described by way of example only and with reference to the drawings in which:

Figure 1:   is a high resolution transmission microscope image of dithioester nanotubes prepared in accordance with the invention;

Figure 2:   is the Raman spectrum of dithioester nanotubes prepared in accordance with the
10   invention, together with the corresponding spectra for pristine carbon nanotubes and acid-treated carbon nanotubes;

Figure 3:   is an X-Ray photoelectron spectrum of dithioester nanotubes prepared in accordance with the invention;

Figure 4:   is another X-Ray photoelectron spectrum of dithioester nanotubes prepared in
15   accordance with the invention;

Figure 5:   is a Fourier transform infrared (FTIR) spectrum of dithioester nanotubes prepared in accordance with the invention – mid-IR range, together with the corresponding spectra for pristine carbon nanotubes, acid-treated carbon nanotubes and dithiopropanoic magnesium chloride;

20   Figure 6:   is a FTIR spectrum of dithioester nanotubes prepared in accordance with the invention – far-IR range, together with the corresponding spectra for pristine carbon nanotubes, acid-treated carbon nanotubes and dithiopropanoic magnesium chloride;

Figure 7:   is a UV spectrum of dithioester carbon nanotubes prepared in accordance with the invention, together with the corresponding spectra for pristine carbon nanotubes,
25   acid-treated carbon nanotubes and dithiopropanoic magnesium chloride; and

Figure 8:   is a micrograph of the results of polymerisation studies using DTE-CNTs of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to a unique approach to the complex functionalisation of carbon nanotubes (CNTs). CNTs are generally considered to be inherently unreactive. The present invention provides a method for the preparation of dithioester carbon nanotubes.

5   As used herein, the term "dithioester carbon nanotube" (DTE-CNT) is intended to mean:
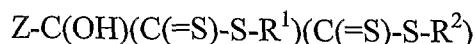
$$Z\text{-}C(OH)(C(=S)\text{-}S\text{-}R^1)(C(=S)\text{-}S\text{-}R^2)$$

wherein Z is a carbon nanotube; and R^1 and R^2 are independently alkyl, alkenyl or aryl, wherein any alkyl, alkenyl or aryl may be optionally substituted.

The DTE-CNTs are suitable for use as chain transfer agents in RAFT polymerisation reactions.
10 In such reactions, the chain transfer agent acts as a free radical trap and provides control over the chain length and, therefore, of the degree of polymerisation.

The carbon nanotubes in the dithioester carbon nanotubes of the invention may be multi-walled (MWCNTs), single-walled (SWCNTs), or double-walled (DWCNTs), or any variants or mixtures thereof. The nanotubes may be doped or undoped.

15 As used herein, the term "alkyl" is intended to include straight chain, branched chain or cyclic saturated hydrocarbon radicals.

As used herein, the term "allyl" is intended to mean the moiety $-CH_2\text{-}CH=CH_2$.

As used herein, the term "alkenyl" is intended to include straight chain, branched chain or cyclic mono-unsaturated hydrocarbon radicals, including allyl and vinyl radicals.

20 As used herein, the term "aryl" is intended to include aromatic radicals including, but not limited to: phenyl; naphthyl; indanyl; biphenyl; and the like.

As used herein, the term "vinyl" is intended to mean the moiety $-CH=CH_2$.

Method of preparation

The dithioester carbon nanotubes are generally prepared by reacting a form of a Grignard reagent
25 with a chemically treated nanotube.

More suitably, the chemically treated nanotube includes a functional moiety that is reactive to a Grignard reagent and the Grignard reagent is a dithiocarboxylated Grignard (DTG).

One preferred embodiment of the invention has the following key steps:

Provision of carbon nanotubes

5   All forms of carbon nanotube are suitable for use in the invention, including single-walled (SWCNTs), double-walled (DWCNTs) and multi-walled (MWCNTs) and any variants and mixtures thereof. Doped carbon nanotubes, in particular boron- and/or nitrogen-doped nanotubes, may also be utilised.

The preparation of carbon nanotubes is well-known to those persons skilled in the art. Suitable
10   methods for preparing carbon nanotubes include, but are not limited to: laser ablation; chemical vapour deposition; and arc discharge. The present invention is not limited to carbon nanotubes produced by any particular method.

In one preferred embodiment, for ease of functionalisation, the carbon nanotubes are formed by chemical vapour deposition.

15   The methods of the present invention are not restricted by dimensions of the carbon nanotubes, or by their quality, quantity, or electronic, mechanical or thermal properties.

Carbon nanotubes of varying diameters may be produced and are readily available. The methods of the present invention have been applied to carbon nanotubes having diameters of between about 10 nm and about 60nm, but the invention is not limited to such carbon nanotubes.

20   *Oxidation of nanotubes*

The carbon nanotubes (CNTs) are generally oxidised to produce moieties on their surface which may be functionalised. Methods for oxidising CNTs are known to those persons skilled in the art and include, but are not limited to: chemical treatment; thermal treatment; ozone treatment; radio frequency oxidation; oxygen plasma oxidation; microwave plasma oxidation; and laser ablation.

25   In one embodiment, the CNTs are oxidised by chemical treatment. Oxidation of CNTs by chemical treatment results in the formation of carboxyl, carbonyl, ether-type and alcohol moieties on the CNT surface.

A preferred method of oxidising CNTs by chemical treatment involves sonicating a suspension of CNTs in an acid or mixture of acids. This method is known in the art as sonochemical oxidation. Suitable acids include, but are not limited to, mixtures of sulfuric (H_2SO_4) and nitric (HNO_3) acids.

5   Sonochemical oxidation of CNTs in H_2SO_4/HNO_3 results in the formation of carboxylic acid (-COOH) and hydroxyl (-OH) functional groups on the surface of the CNTs.

Alternative chemical treatment methods include refluxing a suspension of CNTs in an acid or mixture of acids. The reaction time and reaction temperature may be varied, together with the composition and concentration of the acid or acid mixture.

10   Other chemicals that may be used to oxidise CNTs are know to those persons skilled in the art. They include, but are not limited to: potassium permanganate; potassium dichromate; hydrogen peroxide; oxygen gas; hypochlorite; OsO_2; and super acids, such as: oleum (20% free SO_3); methanesulfonic acid; trifluoromethanesulfonic acid (triflic acid); and chlorosulfonic acid.

The concentration and duration of acid treatment, and the duration and power level of plasma,
15   thermal, microwave or sonication treatment, to give the required level of oxidation of the CNTs, are dependent on the type of CNTs and the method by which they have been produced. Varying these conditions will give differing ratios of oxidation products on the surface of the CNTs which may be required for different applications. In addition, oxidation may cause exfoliation, shortening and modification of the intrinsic properties of the CNTs. Therefore, care must be
20   taken to select the appropriate conditions for the oxidation, depending upon the type of nanotube and the desired end application.

The power level of the sonication and the type of nanotubes will dictate the oxidation products formed at the surface of the CNTs during sonochemical oxidation. CNTs produced by arc-discharge are more graphitic in character and typically require higher power sonication and
25   longer treatment times than CNTs produced by chemical vapour deposition. Typically the order of reactivity is SWCNT>DWCNT>MWCNT.

A person skilled in the art will be able, without undue experimentation and with regard to that skill and this disclosure, to select appropriate reagents and conditions to modify the

methodologies described herein to produce oxidised CNTs suitable for use in the methods of the present invention.

In a particularly preferred embodiment of the present invention, the CNTs are sonochemically oxidised in a mixture of concentrated sulphuric and nitric acids to provide carboxyl-

5   functionalised CNTs. This reaction is illustrated in the first step of Scheme 2.

Scheme 2
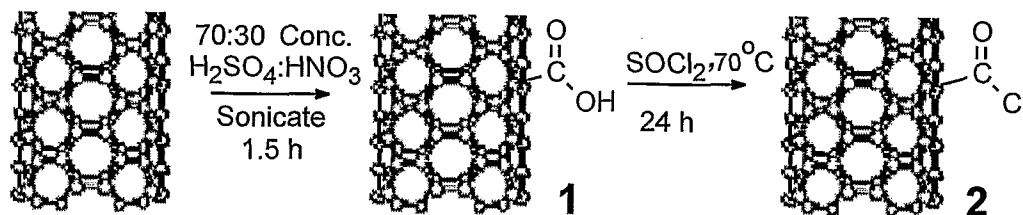
Preparation of functionalised nanotubes susceptible to a Grignard reagent

The surface functional groups on the oxidised CNTs are generally modified to provide moieties

10   that are susceptible to a Grignard reagent. Such moieties are known in the art and include: acyl halides; alkyl halides (primary, secondary and tertiary); aryl halides; alkyl alcohols (primary, secondary and tertiary); aryl alcohols; ketones; aldehydes; anhydrides; alkyl esters and aryl esters.

Methods for modifying CNTs to incorporate these moieties are known in the art — see, for example: Chen *et al.*, *Science* 1998, **282**, 95; Lui *et al.*, *Science* 1998, **280**, 1253; Hiura *et al.*,

15   *Adv. Mater.* 1995, **7**, 275; and Ajayan *et al.*, *Nature* 1993, **361**, 333.

In a preferred embodiment the oxidised CNTs are modified to provide acyl chloride functionalised CNTs. This is also a process known in the art — see, for example: Takolpuckdee *et al.*, *Macromolecules* 2005, **38**, 1057; Chimiak *et al.*, *J. Heteroatom Chemistry* 2002, **13**, 169; and Kano *et al.*, *Curr. Chem.* 2005, **251**, 141.

20   With reference to the second step in Scheme 2, in this preferred embodiment, the surface carboxyl groups of the oxidised CNTs **1** are reacted with thionyl chloride to give acyl chloride groups on the CNTs **2**. The reaction between the oxidised CNTs and thionyl chloride is generally performed at a temperature of between about 70 °C and about 140°C for between about 24 and about 48 hours. The reaction can be performed in, for example, a closed vessel, or in

25   conventional glassware heated with a water bath or under reflux.

Preparation of the Grignard reagent

The Grignard reagent employed in the methods of the present invention is a dithiocarboxylated Grignard reagent (DTG) of formula (II)

$$RC(=S)SMX \quad (II)$$

5   wherein R is alkyl, alkenyl or aryl, wherein any alkyl, alkenyl or aryl may be optionally substituted; M is Be, Mg, Ca, Sr or Ba; and X is Cl, Br or I.

In a preferred embodiment, R is alkyl or aryl.

In a preferred embodiment, M is Mg.

The DTG may be prepared from a conventional Grignard reagent of formula RMX. In one

10   embodiment, the DTG is prepared by reacting a conventional Grignard reagent of formula RMX with an aliphatic disulfide compound of formula $R'S_2$, wherein R' = alkyl. In a preferred embodiment, the DTG is prepared by reacting the conventional Grignard reagent of formula RMX with carbon disulfide (CS_2).

Scheme 3
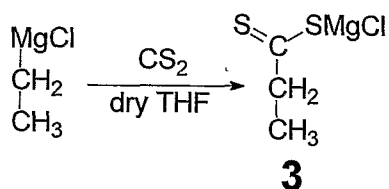
15

Scheme 3 illustrates an example of preparing a DTG according to this preferred embodiment. The DTG, dithiopropanoic magnesium chloride **3**, is prepared by reacting the ethyl magnesium chloride Grignard reagent with CS_2. CS_2 is inserted into the Mg-C bond of the Grignard reagent.

Those persons skilled in the art will be familiar with the preparation and use of conventional

20   Grignard reagents. A number of conventional Grignard reagents of formula RMX are available commercially.

Typically, conventional Grignard reagents wherein M is Mg are prepared by reacting an organic halide with magnesium metal in a suitable solvent. Suitable solvents include, but are not limited to: ethers, such as diethyl ether, methyl *tert*-butyl ether and tetrahydrofuran; glycol diethers;

tertiary amines; toluene; dioxane and hexane. For example, ethylmagnesium bromide may be prepared by heating a mixture of magnesium filings and bromoethane in tetrahydrofuran.

The reaction temperature and time generally depend on the nature of the organic halide. Typically, chlorides are less reactive than bromides or iodides. For alkyl halides, Grignard

5   reagents are most easily prepared from primary halides, followed by secondary halides. It may be difficult to form Grignard reagents from tertiary alkyl halides.

The carbon-metal bond in a conventional Grignard reagent is highly polarised, and the carbon atom is both nucleophilic and basic. The nucleophilic nature of the carbon atom is the basis for rationalising the observed differences in reactivity towards Grignard reagent formation between

10   primary, secondary and tertiary alkyl halides, because the order of reactivity is reversed to that observed for the stability of carbocations.

The polarised carbon atom will react with acids and with a wide variety of electrophiles. Therefore, any optional substituents on the alkyl, alkenyl or aryl group of the DTG must be compatible with the formation of the corresponding conventional Grignard reagent. As will be

15   appreciated by a person skilled in the art, any reactive groups, such as -OH, -NH$_2$ and -CO$_2$H, present on the organic halide must be converted to the corresponding salt, or otherwise modified, before the conventional Grignard reagent can be formed. In addition, groups that react with Grignard reagents, such as hydroxyl groups, carbonyl groups, nitrile groups, esters, nitro groups *etc.*, inhibit Grignard reagent formation entirely and so cannot be present without modification as

20   the optional substituent on the alkyl, alkenyl or aryl group of the DTG.

Those persons skilled in the art will appreciate that those groups that are incompatible with Grignard reagent formation may be protected by protecting groups. Protecting groups may be added and removed in accordance with techniques that are well known to those persons skilled in the art. The use of protecting groups is described in, for example, J. W. F. McOmie (ed.),

25   *Protective Groups in Organic Chemistry*, Plenum Press, London, 1973 and T. W. Greene and P. G. M. Wutz, *Protective Groups in Organic Synthesis*, 2nd edition, Wiley, New York, 1991.

Functional groups that are compatible with Grignard reagent formation are known to those skilled in the art and include, but are not limited to, ether groups and tertiary amine groups.

The complex mechanism of Grignard reagent formation can be completely halted by traces of water. Therefore, all glassware and reagents used to prepare the conventional Grignard reagent and the DTG should be completely dry. To prevent the conventional Grignard reagent or the DTG from reacting with atmospheric moisture, the reaction should performed under dry

5   conditions, advantageously under an inert atmosphere.

Dry conditions also prevent the conventional Grignard reagent from preferentially reacting with water instead of the aliphatic disulfide or CS_2 when preparing the DTG.

The use of ether solvents, such as diethylether or tetrahydrofuran, is thought to stabilise the Grignard reagent. Using tetrahydrofuran instead of diethylether enables the use of higher

10   temperatures in the reaction to form the Grignard reagent. Therefore, the use of tetrahydrofuran is preferred for less reactive halides, such as chlorobenzene.

The quantities of starting materials and solvents should be selected to prevent the solution becoming too concentrated. This is because the polarised carbon atom of the Grignard reagent may react with the organic halide starting material, because the carbon atom to which the halide

15   is attached is nucleophilic.

Formation of the dithioester carbon nanotubes

Grignard reagents will react with a number of moieties, including acyl halides, alkyl and aryl halides, alcohols, ketones, aldehydes, anhydrides and esters. Reacting Grignard reagents with functional groups that comprise a carbonyl generally yields alcohol products.

20   In the method of the present invention, the DTG is reacted with the CNTs carrying a moiety that is susceptible to a Grignard reagent.

In one embodiment, the moiety that is susceptible to a Grignard reagent is an acyl chloride, ester or anhydride.

In a preferred embodiment of the present invention, the DTG is reacted with acyl chloride

25   functionalised CNTs.

In a particularly preferred embodiment, dithiopropanoic magnesium chloride is reacted with acyl chloride functionalised CNTs. This reaction is illustrated in Scheme 4.

Without wishing to be bound by theory, it is believed that this reaction occurs by sequential addition-elimination-addition reactions. The organometallic reagent **3** — the DTG — is a source of a nucleophilic thiol group, which bonds to the electrophilic carbon of the carbonyl group of the acyl chloride functionalised CNT **2**. The chloride is eliminated from the tetrahedral

5   intermediate **4** as its anion. The ketone product of this elimination **5** then adds a second equivalent of the organometallic reagent **3**. The reaction terminates with the hydrolysis of the resulting alkoxide salt to produce the dithioester functionalised carbon nanotube **6**.

Scheme 4
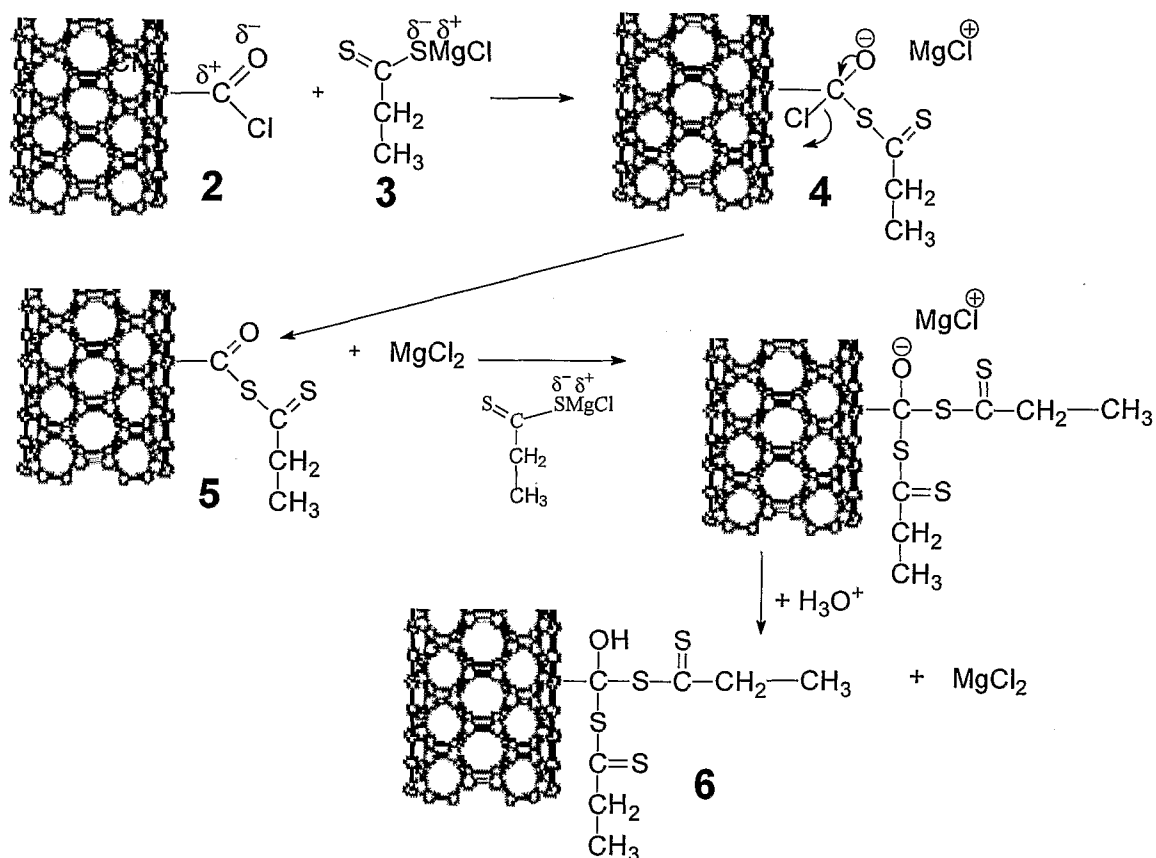
10   In another particularly preferred embodiment, described in the Examples, a phenyl-based DTG (*i.e.* R is aryl) is reacted with acyl chloride functionalised CNTs to produce dithioester functionalised carbon nanotubes.

Properties of the dithioester carbon nanotubes

Typically, pristine CNTs are highly hydrophobic and, as such, are insoluble in most common solvents without modification. Therefore, improving the solubility of CNTs increases the potential for using CNTs in a broader range of applications.

5   Advantageously, the DTE-CNTs of the present invention are water-soluble, unlike the thionyl chloride-treated CNTs. Therefore, the DTE-CNTs of the present invention are potentially useful as chain transfer agents in the preparation of hydrophilic polymer systems by RAFT polymerisation processes. In comparison to non-polar hydrophobic systems, the use of the water-soluble DTE-CNTs of the present invention as chain transfer agents means that biopolymers

10   (formed from biomonomers that undergo free radical polymerisation) and biodegradable polymers can be prepared in RAFT polymerisation processes.

The DTE-CNTs of the present invention are also potentially useful in biological thioacylation reactions, which reactions require hydrophilic systems.

Examples

15   **Synthesis of acyl chloride nanotubes**

SWCNTs (36.9 mg) were ultra-sonicated (60 W) for 1.5 hours in concentrated H_2SO_4/HNO_3 (70:30 v/v). The resulting suspension was filtered under vacuum through a 0.45 μm polytetrafluoroethylene (PTFE) Whatman microfilter paper and thoroughly washed with de-ionised water until the outlet was neutral to pH paper. The acid-treated tubes were dried in a

20   desiccator overnight, then added to thionyl chloride (5 mL) with 4 drops of dimethylformamide (DMF). The resulting suspension was sonicated for 1 minute, then heated in a sealed vessel at 70°C in a water bath for 24 hours. The suspension was then filtered under vacuum through a 0.45 μm PTFE Whatman microfilter and thoroughly washed with anhydrous tetrahydrofuran (THF).

25   **Synthesis of dithiopropanoic magnesium chloride**

Ethyl magnesium chloride (2.0 M in THF, 10.5 mL, 20.1 mmol, Aldrich) was transferred to a 100 mL three-neck round bottom flask under nitrogen. Carbon disulphide (2.30 mL, 30.0 mmol) in dry THF (5 mL) was added drop-wise into the flask over a 15 minute period. The solution

went from a dark purple to an orange/red colour as the dithiopropanoic magnesium chloride formed. The product was used as is in the next stage.

^{1}**H-NMR (D$_2$O/DCl, 298 K, 200 MHz)** δ (ppm from TMS) 1.85 (3H, m, CH$_2$CH$_3$), 4.22 (2H, m, SC(=S)CH$_2$CH$_3$); **FTIR (cm^{-1})** 2964 (CH$_3$ asymmetric stretch), 2920 (CH$_2$ asymmetric stretch),

5   2869 (CH$_3$ symmetric stretch), 2851 (CH$_2$ symmetric stretch), 1300 (S-C=S asymmetric stretch), 1070 (S-C=S symmetric stretch).

Synthesis of dithioester carbon nanotubes (DTE-CNTs)

Dried acyl chloride nanotubes in anhydrous THF (20 mL) were added to the dithiopropanoic magnesium chloride solution (from above) in a 100 mL round bottomed flask. The solution was

10   refluxed for 24 hours and then left to sit overnight. The functionalised nanotubes were collected by filtration through 0.45 µm PTFE Whatman microfilter paper. The nanotubes were washed with dichloromethane, then with de-ionised water, and were dried in a desiccator prior to analysis.

Characterisation of the DTE-CNTs

15   Dithioester functionalised carbon nanotubes of the invention have been characterised by a variety of techniques, including transmission microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), infrared (IR) spectroscopy, including far-IR and near-IR, and by ultraviolet-visible (UV-vis) absorption spectroscopy.

Figure 1 is a high resolution transmission microscope image of dithioester functionalised multi-

20   walled carbon nanotubes. The image shows that the surface of the DTE-CNTs is decorated with amorphous carbon from the -CH$_2$CH$_3$ termini of the dithioester moieties added to the tubes.

Figure 2 presents the results of Raman spectroscopic studies. Figure 2(A) provides the low frequency region of Raman spectra taken at 514.5 nm for: (a) pristine CNTs; (b) acid-treated CNTs; and (c) dithioester carbon nanotubes (DTE-CNTs). Figure 2(B) provides the high

25   frequency region of the Raman spectra for: (a) pristine CNTs; (b) acid-treated CNTs, and (c) DTE-CNTs.

Figure 2(A) shows that the carbon nanotubes are single-walled carbon nanotubes (SWCNTs), as seen by the radial breathing modes centred at 161cm^{-1}. Acid treatment has little or no effect on

the quantity of these SWCNTs other than to remove the out-of-phase radial phonon displacement at 800 cm^{-1} from the E_{2g} and E_{1g} modes in armchair and zig-zag tubes, respectively. Reaction of the acid-treated carbon nanotubes with a dithiocarboxylated Grignard reagent (DTG) results in the emergence of multiple low frequency vibrations at υ/cm^{-1} = 445, 464 (overlapping S=C-S

5   scissor and C-S-C scissor), 516, 597 (S-C stretch + CH$_3$ rock), 766 (CH$_2$ + CH$_3$ rock), 819, 849 (C-S stretch), and 938 (C-C stretch in ethyl). The high frequency region (Figure 2 (B)) shows the extent of disorder in the system given by the $I_{D(\sim1350\ cm-1)}/I_{G(\sim1592\ cm-1)}$ ratios. Initially, the CNTs have a high degree of disordered carbon (I_D/I_G =0.6), present as amorphous carbon. This is preferentially removed during acid treatment as CO$_2$ (I_D/I_G =0.3). Subsequent treatment with the

10   DTG renews disorder, (I_D/I_G =0.6), with new carbonaceous material being attached to the nanotube surface as sp^3 carbon, CH$_2$CH$_3$ termini. The D-band is upward shifted (blue shifted) by 9 cm^{-1} compared with the pristine material. There are two possible reasons which may be responsible for the Raman shift: (a) a phonon confinement effect; and (b) the strain applied by the surface coating (dithioester groups).

15   The XPS spectra of the DTE-CNTs provide evidence of chemical modification. Figure 3 is the XPS spectrum on the C 1s core level of the DTE-CNTs and Figure 4 is the XPS spectrum on the O 1s core level of the DTE-CNTs. The data from these spectra are presented in Table 1.

Table 1

Peak	BE (eV)	FWHM (eV)	assignment
C1	283.84	1.29	
C2	284.60	1.12	graphitic C
C3	285.45	1.50	
O1	530.76	2.00	
O2	532.57	2.18	–C–O–
O3	534.09	2.20	

The carbon C 1s core level spectrum of sp^2 carbon is observed at 284.60 eV (FWHM 1.12 eV).

20   On the higher-binding-energy side, there is a peak at 285.45 eV from sp^3 hybridized carbon. The most interesting feature is an observed low-binding-energy peak at 283.84 eV (a shift of 0.76 eV) indicating an increase in the density of states at the Fermi level, perhaps due to the change in charge relaxation of the excited carbon atom. Without wishing to be bound by theory it is

believed that this arises from the intercalation of dithioester bonds between the graphene sheets and at defect sites, resulting in the reduction in distance between layers (typically ~0.34 nm).

No S 2p signal was observed because the S-C=S bonds appear to be highly photosensitive.

IR data gives further information on the functionalisation of the CNTs, particularly the mid- and
5   far-IR data. Figure 5 is the mid-IR spectra of: pristine SWCNTs; acid-treated SWCNTs; DTE-CNTs; and dithiopropanoic magnesium chloride. Figure 6 is the far-IR spectra of: (a) dithiopropanoic magnesium chloride; (b) pristine SWCNTs; (c) acid-treated SWCNTs; and (d) SWCNTs after reaction with dithiopropanoic magnesium chloride. The inset in Figure 6 is the first derivative of the spectra (a) and (d).

10   Figure 6 shows that the reaction sequence introduces extrinsic features into the far-IR region of the electronic spectrum of SWCNTs. Evidence for intrinsic electronic effects is also observed with small energy gaps introduced into the continuous densities of states (DOS) at the Fermi level as a result of the finite curvature of the SWCNTs. The acid treatment (see Figure 6(c)) has introduced holes into the valence band of the SWCNTs that lead to an increase in the far-IR
15   absorption. The distinct feature centred at 16.2 μm in the far-IR spectrum for the acid-treated SWCNTs may be a result of the introduction of defects, namely oxidised carbon on the nanotubes. After treatment of the acid-treated tubes with dithiopropanoic magnesium chloride, this feature is removed indicating further functionalisation of the tubes, to form DTE-CNTs.

Figure 7 is a UV spectrum of: acid-treated CNTs; dithiopropanoic magnesium chloride (DT-
20   Grignard); DTE-CNTS; and pristine CNTs. The UV data show no absorption maxima in the 200-300 nm region for the pristine CNTs. After acid treatment, a new band appears at 243 nm which is most likely due to defects introduced on the surface as carbon oxidation (–C=O groups) products, as n→π* transitions. This band remains after thiol treatment from thiocarboxyl groups (–C=S). Only a slight blue shift is observed (~1 nm) which may be due to the orbital interactions
25   between the lone pairs of the thiocarbonyl sulphur atoms and the σ* orbitals of the neighbouring –C-OH group.

Polymerisation of DTE-CNTs in 2-hydroxyethylmethacrylate

Dithioester carbon nanotubes were prepared from a phenyl-based dithiocarboxylated Grignard reagent and 10nm diameter MWCNTs using the procedures described above.
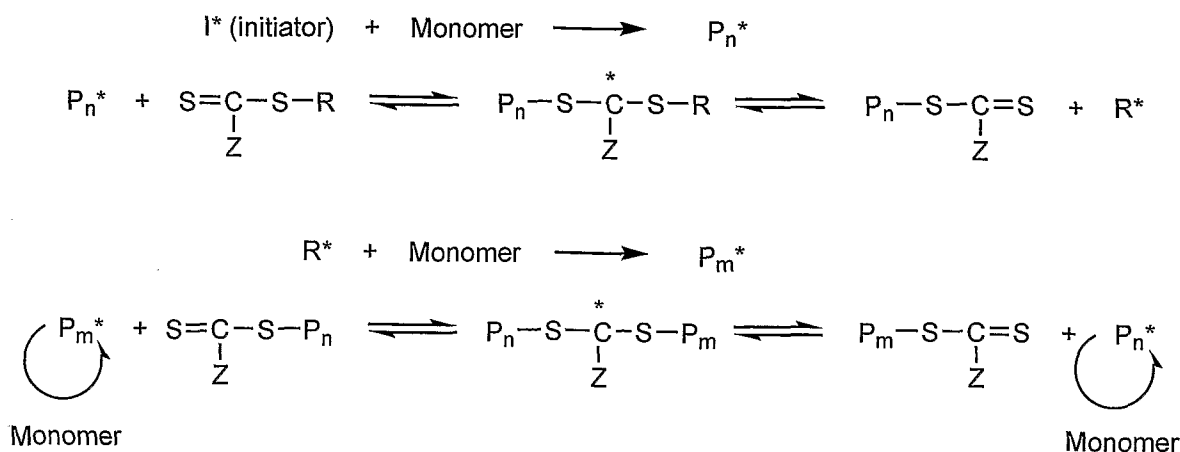
Dithioester carbon nanotubes (10 mg) were added to a solution of 2-hydroxyethylmethacrylate (HEMA) monomer (2 mL) that further included an initiator, typically 2,2-dimethoxy-2-phenylacetophenone (DMPA) (4%, w/w). The resulting mixture was sonicated for 5 minutes, after which it could be drop cast onto a polystyrene, glass or other microscope slide. The slide

5   was placed into a quartz tube, which was purged with nitrogen or argon gas, and exposed to an ultraviolet (UV) lamp for 10-20 minutes or until the composite hardened.

Figure 8(a) is a micrograph of poly(2-hydroxyethyl)methacrylate (PHEMA) after 15 minutes exposure to UV light. The PHEMA appears as a slightly yellow transparent film.

Figure 8(b) is a micrograph of the polymer formed from HEMA monomer to which thionyl

10   chloride-treated MWCNTs (*i.e.* nanotubes with acyl chloride surface moieties) have been added. The polymerisation of this mixture results in the nanotubes clustering together with little or no dispersion in the polymer matrix. This indicates that the nanotubes are not acting as a chain transfer agent and that there is no polymer growth from, or covalent interaction with, the nanotubes' surface.

15   Figure 8(c) is a micrograph of the polymer formed from HEMA monomer to which the dithioester carbon nanotubes (DTE-CNTs) have been added. Figure 8(c) clearly shows that the dispersion of the DTE-CNTs in the PHEMA is superior to the thionyl chloride-treated MWCNTs in Figure 8(b). The film appears slightly yellow and is optically transparent with no clusters of nanotube bundles. This indicates that the DTE-CNTs are acting as a chain transfer agent,

20   separating the nanotubes (*i.e.* there are no van der Waals interactions), and that polymer growth is occurring from individual nanotubes.

Scheme 1

$$I^* \text{ (initiator)} \quad + \quad \text{Monomer} \quad \longrightarrow \quad P_n^*$$

$$P_n^* \quad + \quad \underset{Z}{S=C}-S-R \quad \rightleftharpoons \quad P_n-S-\underset{Z}{\overset{*}{C}}-S-R \quad \rightleftharpoons \quad P_n-S-\underset{Z}{C}=S \quad + \quad R^*$$

$$R^* \quad + \quad \text{Monomer} \quad \longrightarrow \quad P_m^*$$

$$P_m^* \quad + \quad \underset{Z}{S=C}-S-P_n \quad \rightleftharpoons \quad P_n-S-\underset{Z}{\overset{*}{C}}-S-P_m \quad \rightleftharpoons \quad P_m-S-\underset{Z}{C}=S \quad + \quad P_n^*$$

Monomer   Monomer

Therefore, the polymerisation of HEMA monomer in the presence of the DTE-CNTs prepared according to the procedure described above is thought to proceed according to the following mechanism set out in Scheme 1 wherein: monomer = 2-hydroxyethyl methacrylate (HEMA) monomer; Z = CNT; P_n = poly(2-hydroxyethyl) methacrylate (PHEMA); and R= aromatic.

5   Where in the foregoing description reference has been made to elements or integers having known equivalents, then such equivalents are included as if they were individually set forth.

In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognise that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

10   To those skilled in the art to which the invention relates, many changes in construction and widely differing embodiments and applications of the invention will suggest themselves without departing from the scope of the invention as defined in the appended claims. The disclosures and the descriptions herein are purely illustrative and are not intended to be in any sense limiting.

INDUSTRIAL APPLICABILITY

15   As would be envisaged by one skilled in the art, the potential applications of the DTE-CNTs according to this invention are wide-reaching. These include:
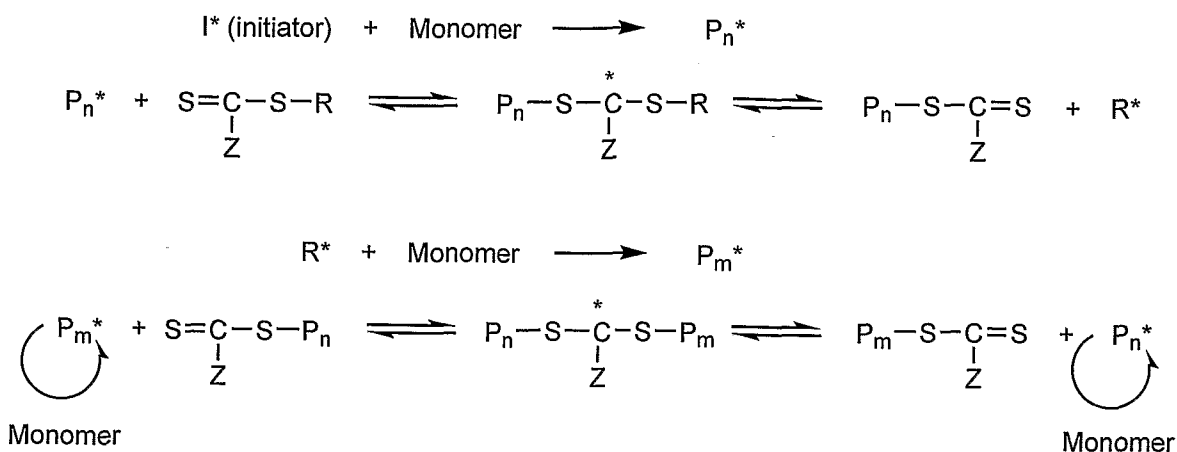
(a)   Bulk production of the DTE-CNTs for use as a chain transfer agent in reversible addition fragmentation chain transfer (RAFT) polymerisations for the manufacture of polymer systems, for example: polyvinyl acetate (PVA); polyacrylamide (PAA); polyvinyl pyrrolidone (PVP); and
20   polymethyl methacrylate (PMMA). In such reactions, the DTE-CNTs act as a free radical trap and provide control over the chain length and, therefore, of the degree of polymerisation.

Scheme 1, which shows the mechanism of a typical RAFT polymerisation, is repeated below for convenience.

The RAFT polymerisation may be performed simply by introducing the DTE-CNT chain transfer
25   agent into an otherwise conventional free radical polymerisation. The effectiveness of the chain transfer agent, S=C(-Z)-S-R, depends on its transfer constant. The transfer constant is determined by the nature of the groups R and Z, where R is a free radical homolytic leaving group that is capable of re-initiating the polymerisation, and Z is a group that governs the activity

of the C=S moiety toward radical addition. The 'living' nature of this polymerisation is evidenced by the retention of a thioester group at the end of the polymer chain — see J. Chiefari *et al.*, *Macromolecules* 1998, **31**, 5559. A wide range of monomers can be used in RAFT polymerisations, including, but not limited to: acrylics; styrenes; acrylamides; and vinyl acetate.

5   **Scheme 1**

$$I^* \text{ (initiator)} + \text{Monomer} \longrightarrow P_n^*$$

$$P_n^* + \underset{\underset{Z}{|}}{S=C}-S-R \;\rightleftharpoons\; P_n-S-\underset{\underset{Z}{|}}{\overset{*}{C}}-S-R \;\rightleftharpoons\; P_n-S-\underset{\underset{Z}{|}}{C}=S + R^*$$

$$R^* + \text{Monomer} \longrightarrow P_m^*$$

$$P_m^* + \underset{\underset{Z}{|}}{S=C}-S-P_n \;\rightleftharpoons\; P_n-S-\underset{\underset{Z}{|}}{\overset{*}{C}}-S-P_m \;\rightleftharpoons\; P_m-S-\underset{\underset{Z}{|}}{C}=S + P_n^*$$

Monomer   Monomer

The use of the DTE-CNTs of the present invention as the chain transfer agent in a RAFT polymerisation provides a polymer-CNT composite.

(b)   Doping of DTE-CNTs into a monomer and then applying an electric field while *in situ*

10   polymerising the mixture to give rise to polymer films in which the CNTs are aligned. These polymer films may be used in a variety of applications such as in: biosensors; field-effect screens; electromagnetic shields; and microfluidic devices.

CLAIMS

1.   A dithioester carbon nanotube (DTE-CNT) of formula (I):

$$Z\text{-}C(OH)(S\text{-}C(=S)R^1)(S\text{-}C(=S)R^2) \quad (I)$$

wherein Z is a carbon nanotube, and R^1 and R^2 are independently alkyl, alkenyl or aryl,

5   wherein any alkyl, alkenyl or aryl may be optionally substituted.

2.   A DTE-CNT as claimed in Claim 1, wherein the DTE-CNT is water-soluble.

3.   A DTE-CNT as claimed in Claim 1 or 2, wherein R^1 and R^2 are both alkyl.

4.   A DTE-CNT as claimed in Claim 1 or 2, wherein R^1 and R^2 are both aryl.

5.   A method of preparing a DTE-CNT comprising the steps of:

10   -   functionalising a CNT with a moiety that is susceptible to a Grignard reagent or a
       modified Grignard reagent to provide a functionalised CNT; and

      -    reacting the functionalised CNT with a dithiocarboxylated Grignard reagent (DTG)
       of formula (II):

$$RC(=S)SMX \quad (II)$$

15   wherein R is alkyl, alkenyl or aryl, wherein any alkyl, alkenyl or aryl may be
       optionally substituted; M is Be, Mg, Ca, Sr or Ba; and X is Cl, Br or I;

      to obtain one or more DTE-CNTs.

6.   A method as claimed in Claim 5, wherein the moiety that is susceptible to a Grignard
      reagent or a modified Grignard reagent is selected from the group consisting of: acyl

20   halides; alkyl halides; aryl halides; alkyl alcohols; aryl alcohols; ketones; aldehydes;
      anhydrides; alkyl esters; and aryl esters.

7.   A method as claimed in Claim 5 or 6, wherein the moiety that is susceptible to a Grignard
      reagent or a modified Grignard reagent is selected from the group consisting of: acyl
   halides; anhydrides; alkyl esters; and aryl esters.

25 8.   A method as claimed in any one of Claims 5 to 7, wherein the moiety that is susceptible to
      a Grignard reagent or a modified Grignard reagent is an acyl halide.

9.   A method as claimed in any one of Claims 5 to 8, wherein the step of functionalising the
      CNT includes the preliminary step of oxidising the CNT.

10. A method as claimed in Claim 9, wherein the CNT is oxidised by chemical treatment.

11. A method as claimed in Claim 9 or 10, wherein the CNT is oxidised with an acid or a mixture of acids.

12. A method as claimed in any one of Claims 5 to 11, wherein the DTG is prepared by reacting a Grignard reagent of formula RMX with an aliphatic disulfide of formula R'S$_2$, wherein R' is alkyl, or with carbon disulfide.

13. A method as claimed in any one of Claims 5 to 12, wherein R is alkyl.

14. A method as claimed in any one of Claims 5 to 12, wherein R is aryl.

15. A method as claimed in any one of Claims 5 to 14, wherein M is magnesium.

16. A method as claimed in any one of Claims 5 to 13 and 15, wherein the DTG is dithiopropanoic magnesium chloride, $CH_3CH_2C(=S)SMgCl$.

17. A method as claimed in claim 16, wherein the dithiopropanoic magnesium chloride is prepared by reacting ethylmagnesium chloride, CH_3CH_2MgCl, with CS_2.

18. A method as claimed in any one of Claims 5 to 17, wherein the DTE-CNT is water-soluble.

19. A DTE-CNT prepared substantially according to the method as claimed in any one of Claims 5 to 18.

20. Use of a DTE-CNT as claimed in any one of Claims 1 to 4 and 19 as a chain transfer agent in a reversible addition fragmentation chain transfer (RAFT) polymerisation.

21. A charge transfer agent, suitable for use in a RAFT polymerisation process, comprising a DTE-CNT of formula (I):

$$Z\text{-}C(OH)(S\text{-}C(=S)R^1)(S\text{-}C(=S)R^2) \quad (I)$$

wherein Z is a carbon nanotube, and R^1 and R^2 independently alkyl, alkenyl or aryl, wherein any alkyl, alkenyl or aryl may be optionally substituted.

22. A charge transfer agent as claimed in Claim 21, wherein the charge transfer agent is water-soluble.

23.   A method of preparing a polymer-CNT composite comprising the steps of:

- providing a charge transfer agent comprising a DTE-CNT of formula (I):

$$Z-C(OH)(S-C(=S)R^1)(S-C(=S)R^2) \quad (I)$$
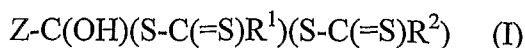
wherein Z is a carbon nanotube, and R^1 and R^2 are independently alkyl, alkenyl or aryl, wherein any alkyl, alkenyl or aryl may be optionally substituted; and

- reacting a monomer with the charge transfer agent in a RAFT polymerisation;

to provide the polymer-CNT composite.

24.   A method as claimed in Claim 23, further comprising applying an external electric field during the RAFT polymerisation to align the CNTs.

25.   A method as claimed in Claim 23 or 24, wherein the DTE-CNT is water-soluble.

26.   A polymer-CNT composite prepared substantially according to the method as claimed in any one of Claims 23 to 25.

27.   A polymer-CNT composite as claimed in Claim 26, wherein the composite is conductive.

28.   A polymer-CNT composite wherein the CNT is, or is derived from, a DTE-CNT of formula (I):
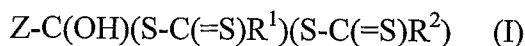
$$Z-C(OH)(S-C(=S)R^1)(S-C(=S)R^2) \quad (I)$$

wherein Z is a carbon nanotube, and R^1 and R^2 are independently alkyl, alkenyl or aryl, wherein any alkyl, alkenyl or aryl may be optionally substituted.

29.   A polymer-CNT composite as claimed in Claim 28, wherein the CNTs are substantially aligned.

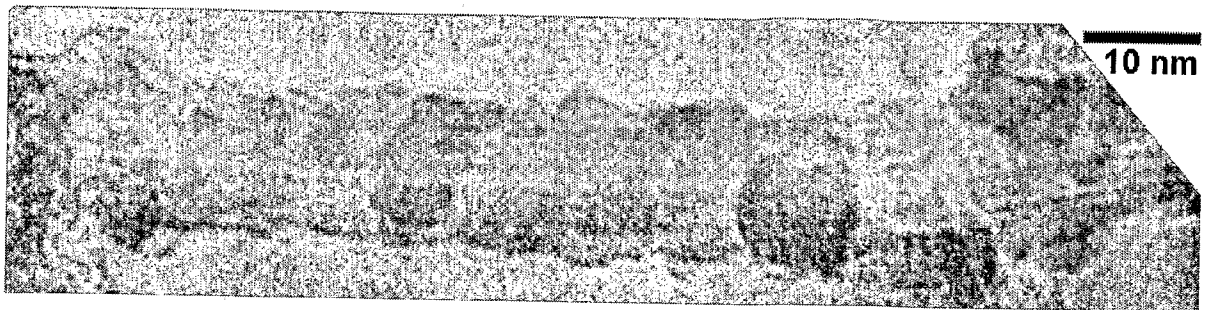30.   A polymer-CNT composite as claimed in Claim 28 or 29, wherein the composite is conductive.
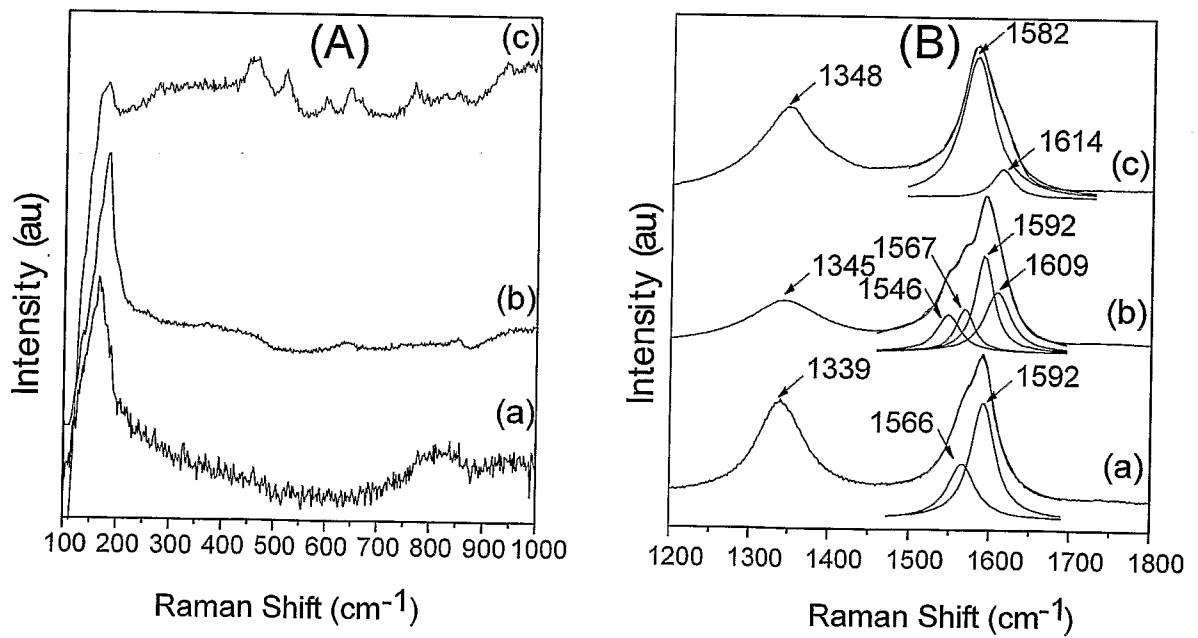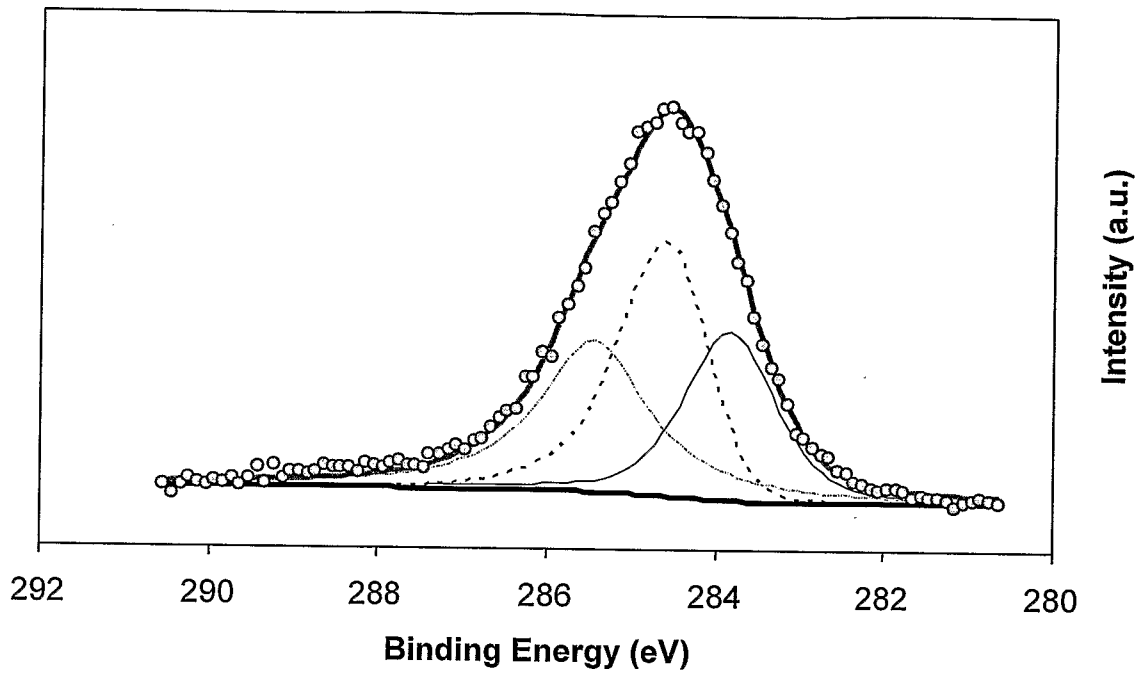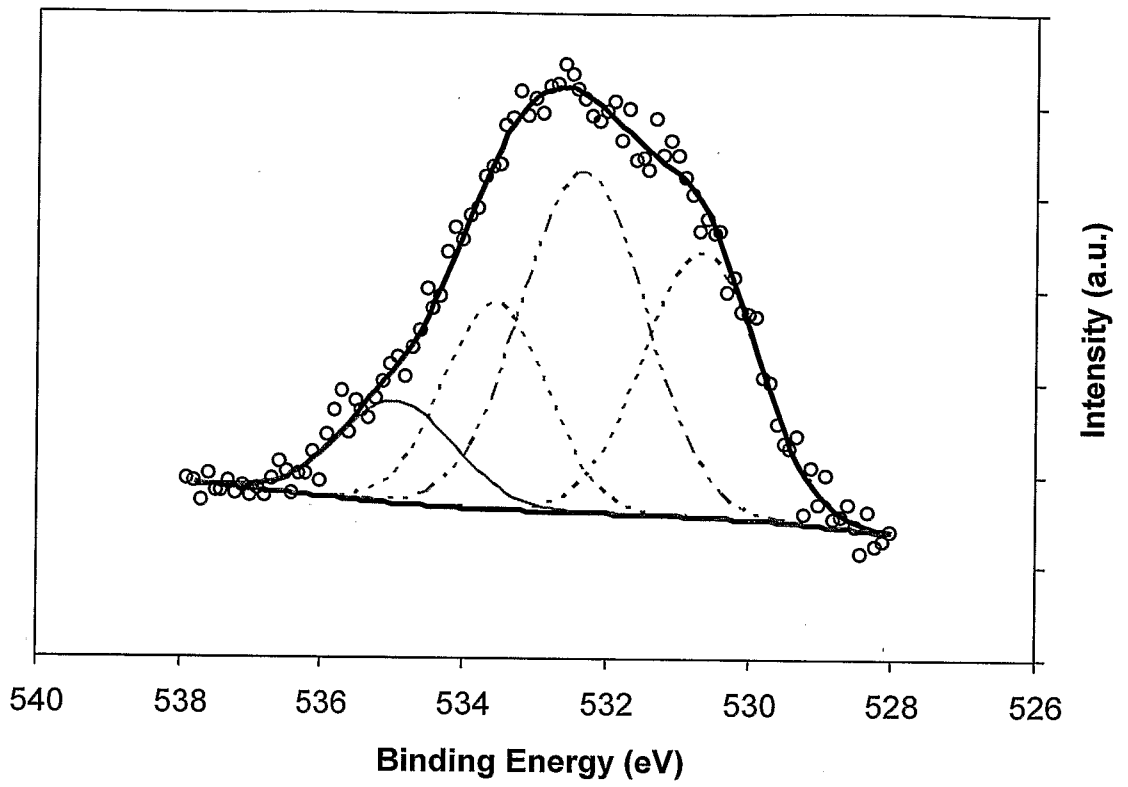
FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4
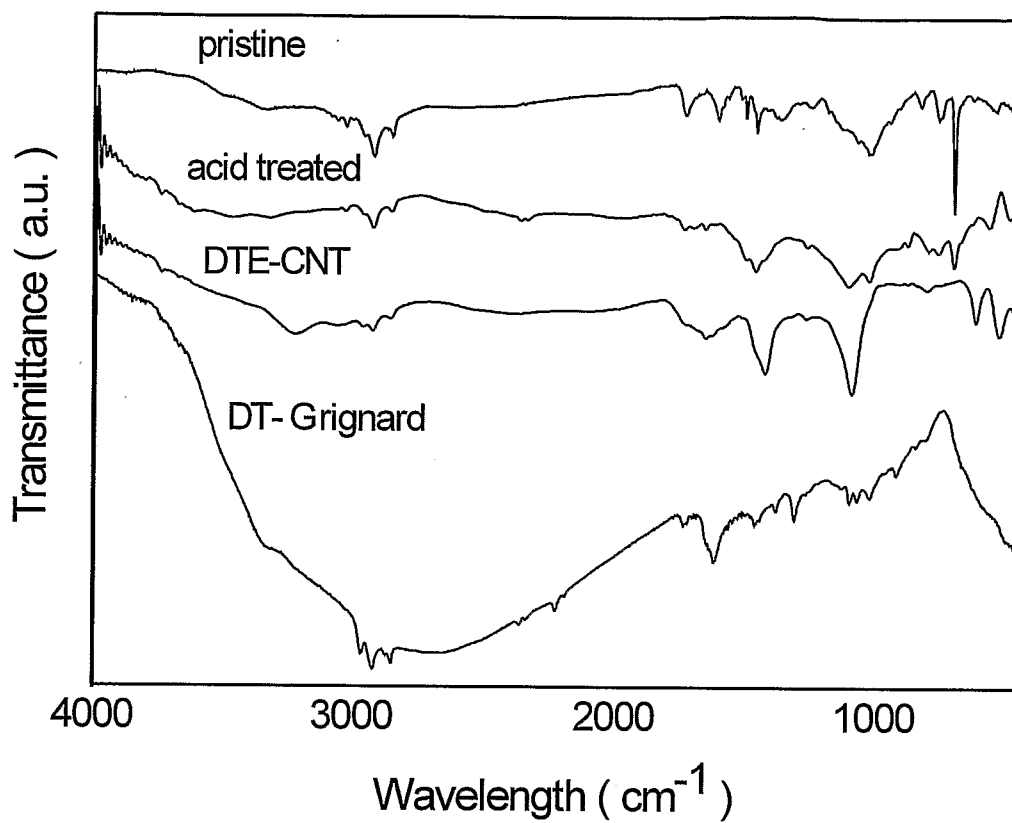
FIGURE 5
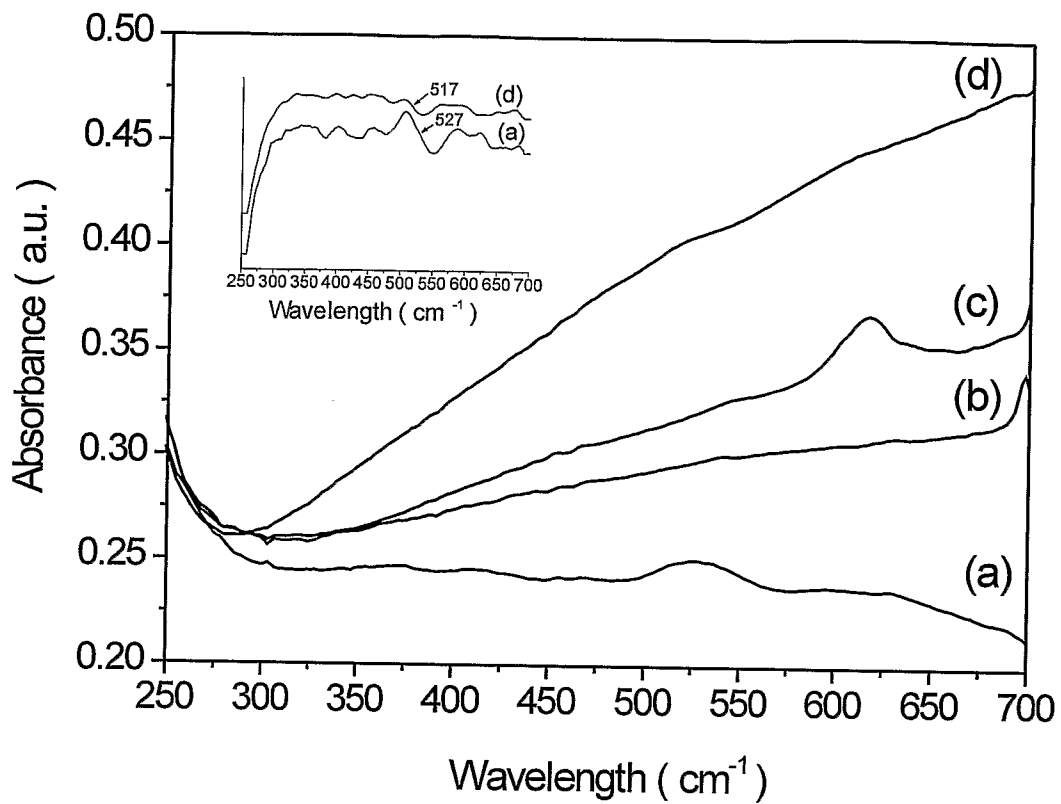
FIGURE 6
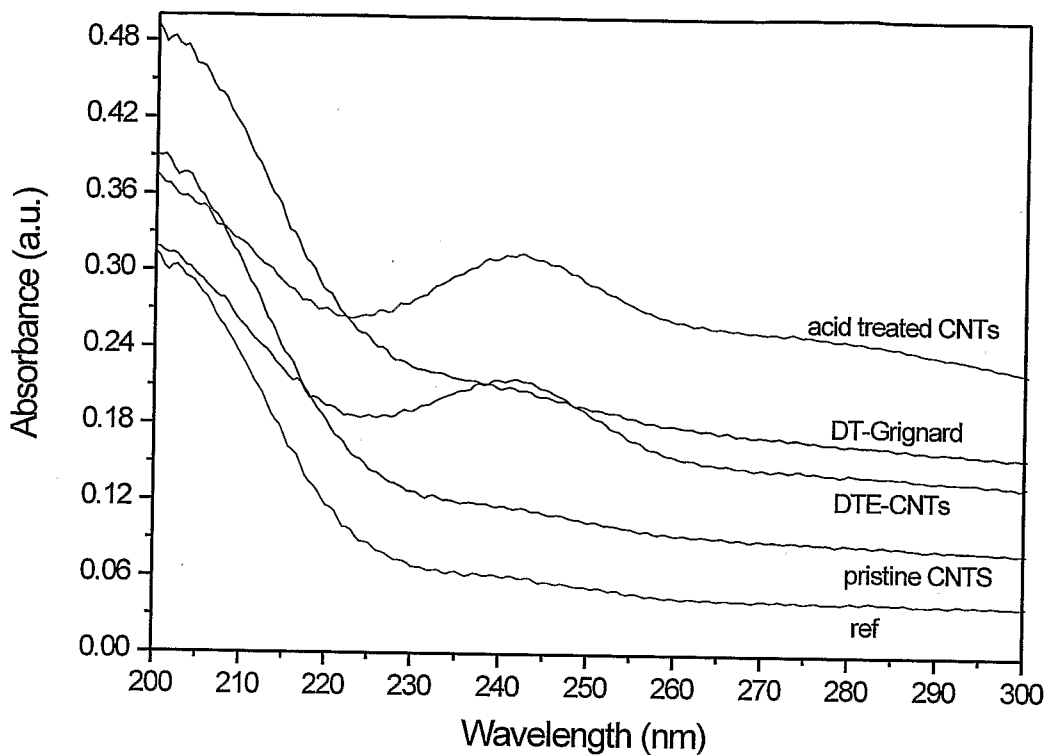
FIGURE 7
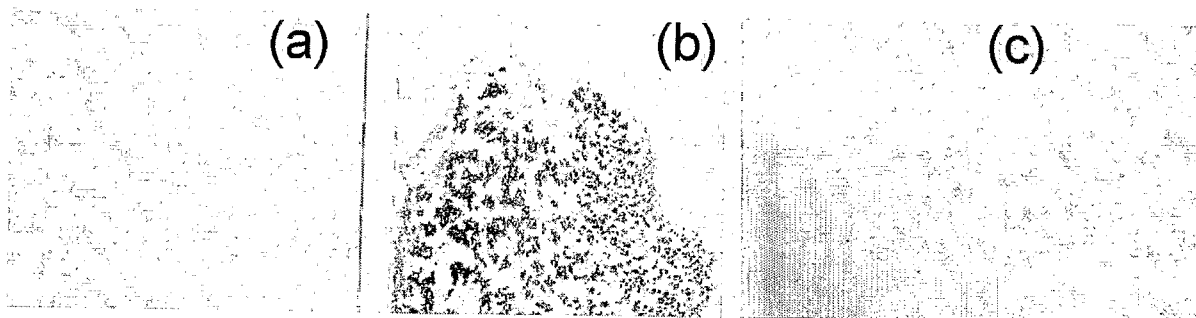
FIGURE 8

A. CLASSIFICATION OF SUBJECT MATTER

B82B 3/00(2006.01)i, C01B 31/02(2006.01)i

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)
  B82B 3/00(2006.01)i, C04B 35/571(2006.01)i, C08K 7/24(2006.01)i, D01F 9/12(2006.01)i

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
  Korean Utility models and applications for Utility models since 1975
  Japanese Utility models and applications for Utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
  eKIPASS(KPA, PAJ, FPD, USPATFULL) in KIPO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2005/030858 A3 (WILLIAM MARSH RICE UNIVERSITY & UNIVERSITY OF HOUSTON) 07 April 2005 see abstract, [0012], [0022] - [0028], claims	1-30
A	US 2004/0223900 A1 (WILLIAM MARSH RICE UNIVERSITY) 11 November 2004 see [0009], [0014] - [0020]	1, 5, 21, 23, 28
A	US 2005/0159293 A1 (General Electric Company) 21 July 2005 see [0002], [0023]	5
A	US 2004/00091114 A1 (William Marsh Rice University) 15 January 2004 see [0022]	5

☐ Further documents are listed in the continuation of Box C.	☒ See patent family annex.

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

Date of the actual completion of the international search	Date of mailing of the international search report
18 APRIL 2007 (18.04.2007)	**18 APRIL 2007 (18.04.2007)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office 920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer KANG, SANG YOON Telephone No. 82-42-481-8153

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		US2004009114A1	15.01.2004
		US2004009114AA	15.01.2004
		US7029646BB	18.04.2006