

Stable compositions of carbon nanotubes - electrolytic polymers

The invention relates to stable compositions of carbon
5 nanotubes and of electrolytic polymers, these electrolytic
polymers being characterized by the presence of phosphonyl
imide or sulfonyl imide functions or alternatively
phosphoric acid functions. The invention also relates to
the manufacture of transparent electrodes comprising these
10 compositions of carbon nanotubes and of electrolytic
polymers.

Carbon nanotubes (CNT) are materials that are very
promising in fields as diverse as high-performance
15 materials and electronics. They exist in the form of
single-walled and multi-walled nanotubes. Unfortunately,
they are difficult to use alone since they are in the form
of aggregates, which especially do not allow light
transmission when, for example, they are deposited onto a
20 support. However, given the size of nanotube fibrils and
their intrinsic conductivity, they are good candidates for
manufacturing transparent electrodes.

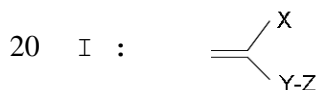
Electrolytic polymers have been widely used in applications
25 as varied as lithium batteries as ionic conductors (K.
Murata, S. Izuchi, Y. Yoshihisa, *Electrochimica Acta* 2000,
45, 1501), for manufacturing organic transistors (A. Malti,
M. Berggren, X. Crispin, *Appl. Phys. Lett.* 2012, 100, 183-
302.), stabilizing magnetite particles (P.L. Golas, S.
30 Louie, G.V. Lowry, K. Matyjaszewski, R.D. Tilton, *Langmuir*
2010, 26, 16890-16900), or as dopants and stabilizers for
the synthesis of conductive polymers (F. Louwet, L.

Groenendaal, J. Dhaen, J. Manca, J.V. Luppen, E. Verdonck, L. Leenders, *Synth. Met.* 2003, 135-136, 115.).

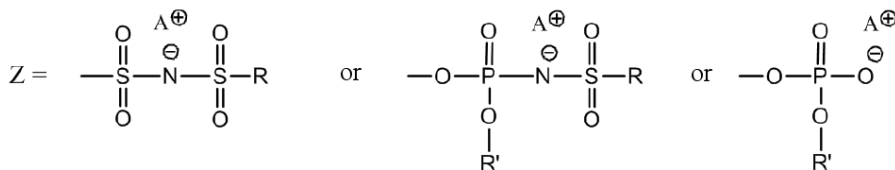
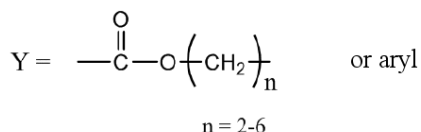
The Applicant has now discovered that certain combinations
 5 of ionic monomers comprising phosphonyl imide or sulfonyl
 imide functions or alternatively phosphoric acid functions,
 in the form of homopolymers or block or non-block
 copolymers, allow good dispersion of CNTs in aqueous
 solutions and that the films obtained using these
 10 dispersions, once the water has evaporated, afford a very
 good transmission-conductivity compromise.

Summary of the invention:

15 The invention relates to a composition comprising carbon
 nanotubes and an electrolytic (co)polymer, this
 electrolytic (co)polymer comprising monomers corresponding
 to formula I.



X = H, CH₃



R = alkyl or F, CF₃, (CF₂)_nF A = H, Li, K, N(R')₄ R' = alkyl, aryl

Detailed description:

The carbon nanotubes used in the invention may be single-walled, double-walled or multi-walled.

5 The electrolytic (co)polymers used in the invention comprise species corresponding to formula (I). They are homopolymers of a species corresponding to formula (I), copolymers comprising at least one species corresponding to formula (I) or alternatively block copolymers in which at
10 least one of the blocks comprises one or more species corresponding to formula (I).

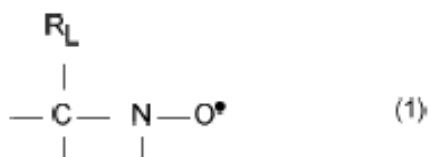
When the electrolytic polymers are copolymers comprising at least one species corresponding to formula (I), the
15 proportion of the species corresponding to formula I represents more than 50% by mass relative to the weight of the copolymer, preferably more than 80% by weight and more preferably more than 90% by weight. The remaining monomer species consist of monomers of any possible type that can
20 undergo radical polymerization.

When the electrolytic polymers are block copolymers, they may be diblock, triblock or multiblock copolymers, provided that at least one of the blocks comprises one or more
25 species corresponding to formula (I), the other blocks comprising monomers that may be chosen from (meth)acrylates, typically acrylic or methacrylic acid, acrylamide, methacrylamide, styrene, N-vinylpyrrolidone, 4-vinylpyridine and more specifically methyl methacrylate,
30 methacrylic acid and styrene.

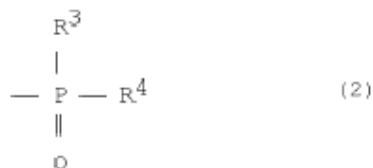
Any chemistry allowing radical polymerization may be used, whether it is controlled or otherwise. Preferably,

nitroxide-controlled radical polymerization or RAFT (radical addition fragmentation transfer), and more preferably RAFT, is used.

- 5 Thus, according to a first aspect of the invention, controlled radical polymerization is performed starting with alkoxyamines derived from the stable free radical (1).



- in which the radical R_L has a molar mass of greater than
 10 15.0342 g/mol. The radical R_L may be a halogen atom such as chlorine, bromine or iodine, a linear, branched or cyclic, saturated or unsaturated hydrocarbon-based group such as an alkyl or phenyl radical, or an ester group $-\text{COOR}$ or an alkoxy group $-\text{OR}$, or a phosphonate group $-\text{PO}(\text{OR})_2$, provided
 15 that it has a molar mass of greater than 15.0342. The monovalent radical R_L is said to be in the β position relative to the nitrogen atom of the nitroxide radical. The remaining valency positions of the carbon atom and of the nitrogen atom in formula (1) may be bonded to various
 20 radicals such as a hydrogen atom, a hydrocarbon-based radical such as an alkyl, aryl or arylalkyl radical, comprising from 1 to 10 carbon atoms. It is not excluded for the carbon atom and the nitrogen atom in formula (1) to be linked together via a divalent radical, so as to form a
 25 ring. Preferably, however, the remaining valency positions of the carbon atom and of the nitrogen atom of formula (1) are linked to monovalent radicals. Preferably, the radical R_L has a molar mass of greater than 30 g/mol. The radical R_L may have, for example, a molar mass of between 40 and
 30 450 g/mol. By way of example, the radical R_L may be a radical comprising a phosphoryl group, said radical R_L possibly being represented by the formula:



in which R³ and R⁴, which may be identical or different, may be chosen from alkyl, cycloalkyl, alkoxy, aryloxy, aryl, aralkyloxy, perfluoroalkyl and aralkyl radicals, and may
 5 comprise from 1 to 20 carbon atoms. R³ and/or R⁴ may also be a halogen atom such as a chlorine or bromine or fluorine or iodine atom. The radical R_L may also comprise at least one aromatic ring as for the phenyl radical or the naphthyl radical, the latter possibly being substituted, for example
 10 with an alkyl radical comprising from 1 to 4 carbon atoms.

More particularly, the alkoxyamines derived from the following stable radicals are preferred:

- N-tert-butyl-1-phenyl-2-methylpropyl nitroxide,
- 15 - N-tert-butyl-1-(2-naphthyl)-2-methylpropyl nitroxide,
- N-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide,
- N-tert-butyl-1-dibenzylphosphono-2,2-dimethylpropyl
 20 nitroxide,
- N-phenyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide,
- N-phenyl-1-diethylphosphono-1-methylethyl nitroxide,
- N-(1-phenyl-2-methylpropyl)-1-diethylphosphono-1-
 25 methylethyl nitroxide,
- 4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy,
- 2,4,6-tri-tert-butylphenoxy.

The alkoxyamines used in controlled radical polymerization
 30 must allow good control of the sequence of monomers. Thus, they do not all allow good control of certain monomers. For example, the alkoxyamines derived from TEMPO make it possible to control only a limited number of monomers, and

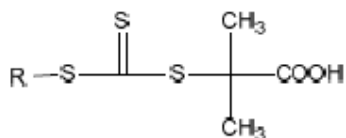
this is likewise the case for the alkoxyamines derived from 2,2,5-trimethyl-4-phenyl-3-azahexane 3-nitroxide (TIPNO). On the other hand, other alkoxyamines derived from the nitroxides corresponding to formula (1), particularly those
 5 derived from the nitroxides corresponding to formula (2) and even more particularly those derived from N-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide, make it possible to broaden to a large number of monomers the controlled radical polymerization of these monomers.

10

In addition, the opening temperature of the alkoxyamines also has an influence on the economic factor. The use of low temperatures will be preferred to minimize the industrial difficulties. A preference will thus be given to
 15 alkoxyamines derived from the nitroxides corresponding to formula (1), particularly those derived from the nitroxides corresponding to formula (2) and even more particularly those derived from N-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide to those derived from TEMPO or
 20 2,2,5-trimethyl-4-phenyl-3-azahexane 3-nitroxide (TIPNO).

According to a second aspect of the invention, which is the preferred mode, the controlled radical polymerization takes place via RAFT, and more particularly with an RAFT agent
 25 corresponding to formula 2 below:

2:



in which R represents an alkyl group comprising 1 to 22 carbon atoms and preferably 10 to 18 carbon atoms.

30

The synthesis of block copolymers may be performed by first preparing the macro-initiator polyelectrolyte block and then, in a second stage, the monomers of the second block may be polymerized, optionally accompanied by other steps

for synthesizing other blocks taking into account other monomers. A macro-initiator block may also be prepared via any other chemistry (anionic, cationic, ring-opening, polycondensation) including one or two end groups allowing
5 the subsequent priming of the monomers comprising the species (I).

Numerous combinations may thus be obtained, for instance in the case of diblock copolymers, hydrophilic-hydrophilic,
10 hydrophilic-hydrophobic, anionic-neutral, anionic-anionic, anionic-cationic or cationic-neutral diblocks.

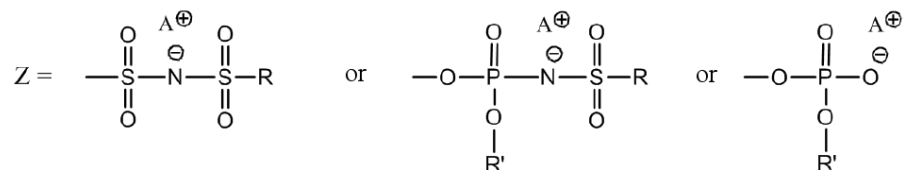
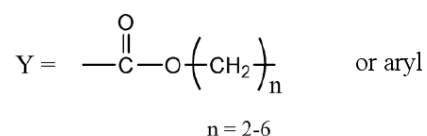
These electrolytic polymers are used in practice for dispersing single-walled or multi-walled carbon nanotubes
15 in electrolytic polymer-CNT mass ratios ranging from 1:10 to 10:1 and preferably from 1:10 to 1:1. The aqueous dispersions of these compositions are stable. They may be placed in the form of thin films via techniques such as spray coating or roll-to-roll for large surfaces. The films
20 derived from these preparations have good electrical conductivity, good optical transmission, good heat stability and also good mechanical properties. They can advantageously replace indium titanium oxide (ITO) as transparent electrode in the fields of optoelectronics and
25 more particularly OLEDs (organic light-emitting diodes) or alternatively photovoltaic organic cells.

These electrolytic polymers may also be used alone, i.e. without CNTs, in the manufacture of membranes that are
30 useful for fuel cells, as ionic conductors or alternatively as stabilizers for particles other than CNTs.

Claims

1. Composition comprising carbon nanotubes and an electrolytic (co)polymer, this electrolytic (co)polymer comprising monomers corresponding to formula I.

X = H, CH₃



R = alkyl or F, CF₃, (CF₂)_nF A = H, Li, K, N(R')₄ R' = alkyl, aryl

2. Composition according to Claim 1, in which the (co)polymer is a homopolymer.
3. Composition according to Claim 1, in which the (co)polymer is a statistical copolymer.
4. Composition according to Claim 1, in which the (co)polymer is a block copolymer.
5. Composition according to Claim 1, in which the carbon nanotubes are single-walled.
6. Composition according to Claim 1, in which the carbon nanotubes are multi-walled.

7. Composition according to Claim 1, in which the copolymers are prepared by controlled radical polymerization.

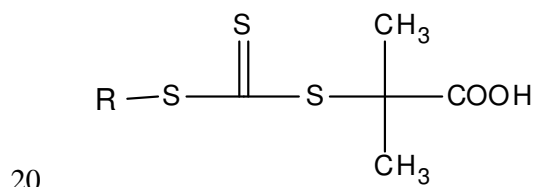
5 8. Composition according to Claim 7, in which the copolymers are prepared by nitroxide-controlled radical polymerization.

9. Composition according to Claim 8, in which the
10 nitroxide is N-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide.

10. Composition according to Claim 7, in which the copolymers are prepared by RAFT-controlled radical
15 polymerization.

11. Composition according to Claim 10, in which the RAFT agent corresponds to formula 2 below:

2 :



in which R represents an alkyl group comprising 1 to 22 carbon atoms.

25 12. Conductive transparent electrode obtained using a composition according to one of Claims 1 to 11.

13. Use of the transparent electrode according to Claim 12 in the fields of OLEDs (organic light-emitting diodes) or
30 in photovoltaic organic cells.