Poly(amino-methacrylate) as versatile agent for carbon nanotube dispersion: an experimental, theoretical and application study

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Carbon nanotubes (CNTs) dispersion in aqueous and organic media was studied in presence of poly(*N*-(2-(dimethylamino) ethyl)-methacrylate) (PDMAEMA). Theoretical and experimental studies were performed in order to emphasize the CNT···PDMAEMA character of the interactions. The rationalization of a CH···π interaction was fully supported by molecular dynamics simulations and confirmed the potential role of PDMAEMA to behave as anchoring agent toward the CNTs. This efficient strategy was applied to the formation of polylactide-based CNTs nanocomposite materials, targeting biomedical applications.

Introduction

The unique structural, electronic and mechanical properties of carbon nanotubes (CNTs) make them of particular interest for applications in materials science, nanotechnologies and medicinal chemistry.[1] However, these promising building blocks present a marginal dispersion in any solvents since CNTs are arranged in bundles due to strong π–π interactions and high aspect ratio. Therefore, different strategies based on covalent and non-covalent functionalization[2] have appeared as a prerequisite for the desagglomeration of CNTs and their widespread use in nanoscience. The surface modification through a supramolecular approach represents certain advantages over the preservation of their conjugated structure, and consequently the intrinsic properties of CNTs. For instance, these modified CNTs maintain their high electronic conductivity, robust mechanical behavior and their potential biosensing properties.[3] In this regard, the effective CNTs dispersion (or solubilization) in organic or aqueous media has mainly been achieved by π–π stacking between pyrene-containing compounds and the CNT surface.[4] Other strategies based on dipole/dipole electrostatic interactions, cation-π interactions and amine-aromatic charge transfer have been developed, aimed at disassembling CNTs bundles.[5]

Poly(2-(*N*,*N*-dimethylamino) ethyl methacrylate) (PDM AEMA) is a biocompatible polymer, exhibiting very high pH- and thermal sensitivity. The sensing ability of PDMAEMA has found some applications as nanofiltration membranes[6] or polycations for gene transfection.[7] In the same way, copolymers comprising PDMAEMA blocks have been synthesized for pH-sensitive hydrogels,[8] paints,[9] and gene delivery systems.[10]

In this context, PDMAEMA appears a good candidate for the non-covalent binding of CNTs due to the pH-induced switching of its ammonium/amine pending groups. For the first time to our knowledge, this study has shown the capability of PDMAEMA to maintain a homogeneous dispersion of CNTs in aqueous media, but also in organic solvents upon both ammonium-π and $(CH_3)_2N$-π non-covalent interactions provided by PDMAEMA. In addition to direct visualization, the nature and the strength of interaction evolved for the CNTs dispersion has been established by ^{1}H NMR analyses and force field-based molecular modeling. For the nanotube dispersion in water, we first studied the strength of interactions between the protonated dimethylamino groups of PDMAEMA and the unsaturated π-system of CNTs at different pH, but also with the corresponding poly[2-(methacryloyloxy)ethyl trimethylammonium iodide] PMETAI. The CNTs dispersion mediated by neutral PDMAEMA was subsequently established in organic solvents. Thanks to these encouraging results, CNTs dispersion in organic solvents has been enlarged to include PDMAEMA-based copolymers, *i.e.*, well-defined poly[(L,L-lactide)-*b*-poly(*N*-(2-dimethylamino) ethyl methacrylate)] diblock copolymers.[11] This strategy is shown to broaden the processing of CNTs-containing biomaterials elaborated with biodegradable poly(L,L-lactide) (PLA).

Results and discussion

The synthesis of poly(*N*-(2-(dimethylamino) ethyl)-methacrylate) was performed by atom transfer radical polymerization (ATRP), this synthetic method provided a control over macromolecular parameters with a low polydispersity index (PDI). 2-(*N*,*N*-Dimethylamino) ethyl methacrylate was polymerized from ethyl α-bromoisobutyrate in presence of CuBr and hexamethylenetetramine (HMTETA) in THF to give the corresponding PDMAEMA **1** in 70% yield. The relative number-average molecular weight (M_n) as obtained by GPC with poly(methyl methacrylate) (PMMA) as reference standard, was determined to be around 11500 g mol^{-1} with a PDI of 1.40 (Fig. 1).

In order to explore the CNTs dispersion in water, we investigated the PDMAEMA-nanotube interactions as a function of pH.[12] Indeed, the aminated side–chains of PDMAEMA can adopt different conformations according to the environment. Under acidic conditions, the macromolecular backbone displays an extended structure due to interactions between the protonated

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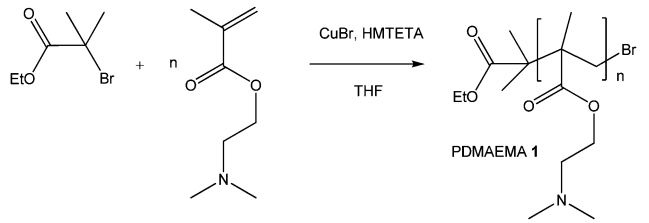

Fig. 1 Synthesis of PDMAEMA **1** by ATRP.

amines and the aqueous media; this open conformation is also supplemented by electrostatic repulsion of the ionic parts. Therefore, the positive charges pending along the chain can be easily available for a "recognition" process with the CNTs π-system. Under basic conditions (pH > 8), the marginal water solubility of PDMAEMA is mainly caused by hydrogen bonding between water molecules and polar functions of the polymer. In this conformation, we could expect that the side chains are mostly back-folded and the residual ammonium species do not ensure strong interactions with CNTs. These data have prompted us to operate the PDMAEMA-CNTs dispersion system at pH 3, 8 and 11. The acidic solution (pH 3) was obtained by adding a few drops of concentrated HCl, and the basic solution (pH 11) was made with saturated sodium carbonate solution. These conditions are known to prevent any ester bond cleavage.[11] The mixtures contained 100 mg of polymer **1** and 5 mg of CNTs in 10 mL of water adjusted at the studied pH. This content in CNTs is commonly used when concerned with CNT-based nanocomposites.[1] After overnight stirring at room temperature, the resulting mixtures were centrifugated at 4000 rpm for 10 min. This set of experiments led to dramatic variations of stabilization, as illustrated in Fig. 2. At pH 11, the solution remained colorless with a complete sedimentation of CNTs. This behavior was attributed to the absence of protonated amine functional groups, which impeded the solubility of polymer **1** in the aqueous media. By proceeding with the PDMAEMA **1** used in its present form (pH 8), the mixture showed a slightly dark color. In this case, residual hydrogen bonds could link the dimethylamino groups to the unsaturated surface of CNTs and generate their partial solubilization in water. Finally, under acidic conditions, amine groups pending along the PDMAEMA chain were protonated, giving rise to a high ratio of ammonium functional groups and good solubility in water. Thus, the enrichment in cationic species was emphasized by the dispersion of a large amount of CNTs in water; the resulting solution revealed stable behavior over a period as long as two months (no sedimentation was observed).

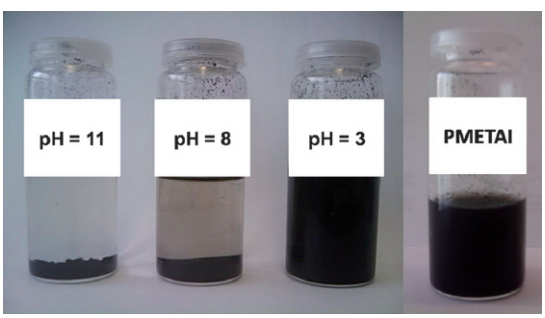

Fig. 2 Dispersion of MWCNTs in water in presence of PDMAEMA **1** at pH 11, pH 8 and pH 3 (left) and PMETAI **2** (right).

These results show that cation-π interactions occurred in the system and the amount of dispersed CNTs in water was closely related to the quantity of cationic units.

However, cooperation between the hydrogen bonding and the $-N^+(CH_3)_2H$-π interactions could occur in the case of PDMAEMA **1**/CNTs system in water at pH 3. Indeed, it is well-established that an unsaturated system can interact with an ammonium function through hydrogen bonding.[13] Therefore, we decided to elucidate the cation-π character of interaction with poly[2-(methacryloyloxy)ethyl trimethylammonium iodide] (PMETAI) **2**. The choice was motivated by the presence of ammonium units bearing four alkyl groups and the very high solubility of PMETAI in water. Compound **2** was prepared by quaternization of polymer **1** with methyl iodide in chloroform at room temperature. Subsequent precipitation in ether yielded the salt **2** in pure form. The polymeric chains **1** and **2** possess a similar backbone, but the role played by the types of ammonium groups ($-N^+(CH_3)_2H$ in **1** and $-N^+(CH_3)_3$ in **2**) are different. A dispersion test was performed with 100 mg of polymer **2**, 5 mg of CNTs in 10 mL of water. After being vigorously stirred overnight, successive centrifugation and filtration steps afforded a deeply black solution, which was stable over a period of two months (CNTs sedimentation was not observed). The presence of ammonium units in **2** allowed a good dispersion of CNTs, taking place owing to $-N^+(CH_3)_3$-π interactions.

At this stage, it has been evidenced that PDMAEMA chains are particularly tailored to the formation of homogeneous CNTs solutions in water. These results have prompted us to study the CNTs dispersion in organic solvents with neutral PDMAEMA **1**.

First, we decided to compare the ammonium-π/amine-π interactions through the CNTs dispersion in methanol with PDMAEMA **1** and PDMAEMA.HCl **3**, these polymers exhibited high-solubility in this solvent. The salt **3** was obtained by quaternizating the polymer **1** in a hydrochloride chloroform solution. This technique provided the corresponding PDMAEMA.HCl salt **3** in dry form, suitable for a test of CNTs dispersion in water-free organic solvent. The ^{1}H NMR analysis in methanol-D_4 has confirmed the protonation of dimethylamino pending groups. The $-CH_2N$ = methylene protons of starting material **1** shifted from 2.65 to 3.62 ppm, and the $(CH_3)_2N-$ methyl groups have moved from 2.33 to 3.05 ppm, consistent with a stronger electron-withdrawing effect of the nitrogen due to protonation. A downfield shift of 0.30 ppm was also observed for the $-CH_2O-$ methylene and a minor variation was seen for the other groups (Fig. 3).

The comparison between PDMAEMA **1** and PDMAEMA.HCl **3** as dispersing agents was carried out under the experimental conditions depicted in the previous case, namely a mixture of 100 mg of polymer **1** or **3**, 5 mg of CNTs in 10 mL of methanol. The resulting experiments revealed a similar effect for the polymeric substances **1** and **3**, *i.e.*, a deeply dark solution, consistent with a high concentration of finely dispersed CNTs. After cotton-filtration for removal of CNTs excess, the resulting methanolic solutions continue to display a persistent dark color, confirming the homogeneous and stable character of the

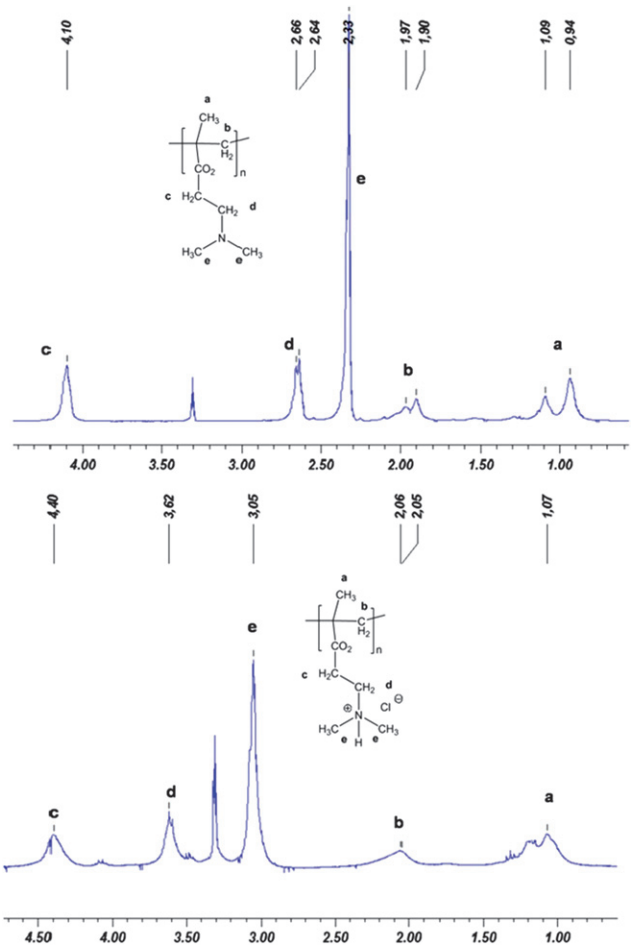

Fig. 3 ^{1}H NMR spectrum of PDMAEMA **1** (top) and PDMAEMA.HCl **2** (bottom) in CD_3OD.

solubilization. No sedimentation was observed over a period of three months. Finally, the PDMAEMA **1** triggered a significant dispersion ability of CNTs under neutral form, which opened up some attractive perspectives for the formation of PDMAEMA templated nanomaterials.

In order to establish the potential control in organic medium, our investigation was undertaken with conventional organic solvents such as ethanol, acetone, THF and chloroform. The experimental conditions mirrored those achieved in the previous cases. When mixtures were carried out in ethanol, THF and chloroform, a persistent dark solution was observed after filtration of CNTs excess. In acetone, a reasonable amount of CNTs was dispersed, but the stability of the dispersion appeared slightly lower with time.

Transmission electron microscopy (TEM) analysis was performed on the homogeneous dispersion of CNTs mediated by PDMAEMA after filtration of the chloroform solution and slow evaporation of the solvent (Fig. 4). It revealed the complete dispersion of CNTs with the presence of some individual CNTs, attesting that PDMAEMA is able to break the CNTs bundles.

The resulting system was also studied by TGA and compared to pure PDMAEMA **1** (Fig. 5). In both cases, the degradation profile showed the same trend. The main first degradation starts at 270 °C for PDMAEMA and at 280 °C for PDMAEMA/

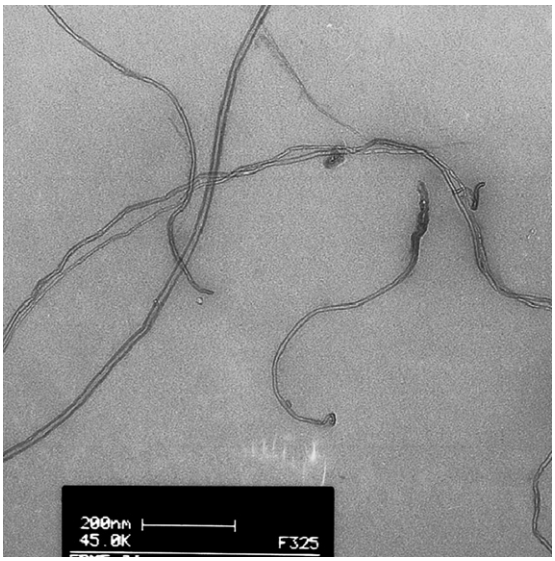

Fig. 4 TEM image obtained from a chloroform suspension of CNTs with PDMAEMA **1**.

CNTs. The weight of the residues left for PDMAEMA and PDMAEMA/CNTs was close to 3 and 6%, respectively.

To address the issue of how PDMAEMA **1** interacts with the unsaturated structure of CNTs, ^{1}H NMR spectroscopy appeared as the appropriated tool for elucidating the bonding sites of the polymeric chain.

According to the previously described protocol, a mixture of PDMAEMA **1** and CNTs was prepared in $CDCl_3$ at room temperature. After filtration of the CNTs excess, the resulting solution was monitored by ^{1}H NMR. The main change between both spectra was located in the region corresponding to the methyl groups of the polymer backbone (Fig. 6). In pure PDMAEMA, three peaks were observed and assigned to the methyl groups corresponding to mm, mr, and rr triad resonances, namely 1.24, 1.04 and 0.88 ppm, respectively (Fig. 6 top). In the case of PDMAEMA/CNTs, a significant intensity increase of the peak at 1.24 ppm is interestingly observed, suggesting a higher mobility of isotactic triads (Fig. 6 bottom). It is worth noting that the functional groups adsorbed on the CNTs have a lower mobility with respect to pure PDMAEMA and therefore,

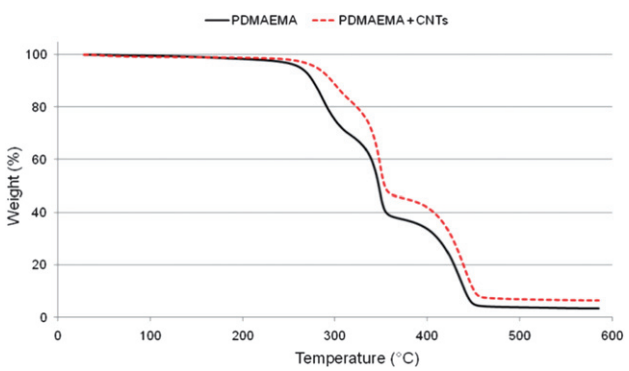

Fig. 5 TGA of PDMAEMA **1** (bold line) and PDMAEMA/CNTs (dotted line) under air.

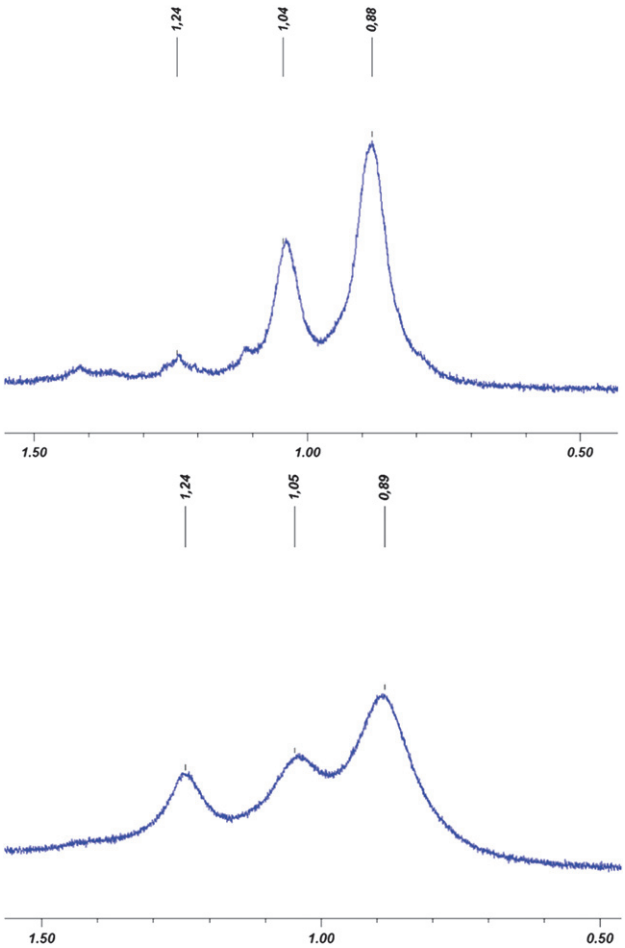

Fig. 6 ^{1}H NMR spectra in $CDCl_3$ of PDMAEMA **1** (top) and PDMAEMA/CNTs (bottom).

these segments should give a low signal in ^{1}H NMR. The increase in the relative intensity of the peak at 1.24 ppm suggests that mm triads have a higher mobility than their mr and rr counterparts in the polymer chains adsorbed on the CNT. In our hypothesis, bonding between PDMAEMA **1** and the CNTs may be produced by interactions involving the amine groups and the unsaturated π-system, arising from particular conformations adopted by the polymer chain on the nanotube surface. However, the determination *via* NMR spectroscopy of selective interactions between mr and rr triads and the unsaturated π surface remains challenging.

In order to determine the organization of the PDMAEMA chains around the CNT, as reflected in the NMR data (Fig. 6), and the nature of the interactions between the two materials, we studied this system by force field-based molecular modeling. In particular, molecular dynamic (MD) simulations were performed to investigate the conformational behavior of PDMAEMA interacting with CNTs. As a model system, a single isotactic chain of PDMAEMA was brought in the vicinity of an infinite, armchair, single wall carbon nanotube (SWNT). The presence of a solvent (chloroform) was taken implicitly into account by considering a surrounding medium with its dielectric constant. Three different models were built, combining polymer chains with a different number of monomer

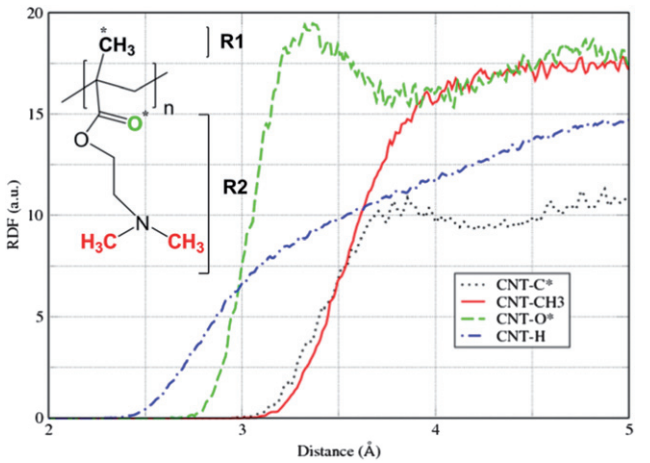

Fig. 7 Monomer unit of PDMAEMA (left). The two substituents are indicated as R1 and R2; (right) plot of the RDFs calculated over 600 ps for model **(b)**. The onset of the RDF curves indicate the shortest distance between the CNT and the considered atoms.

units, *l*, and SWNTs with a different index *n*: (a) $l = 20$, $n = 10$; (b) $l = 50$, $n = 10$ and (c) $l = 50$, $n = 20$ where *n* corresponds to the first chiral index.[14] In order to investigate the possibility that the change in the NMR spectrum of PDMAEMA upon interaction with CNTs arises from particular conformations adopted by the polymer chain on the nanotube surface, radial distribution functions (RDFs) were calculated between the carbon atoms in the CNT and atoms in different locations in the monomer units.

Referring to the notation in Fig. 7 (left), the following RDFs were calculated: CNT-H (all hydrogen atoms), CNT-O* (the doubly-bonded oxygen atoms), CNT-*CH_3 (the carbon of the methyl group along the backbone), CNT-CH_3 (the carbon atoms of the dimethylamino groups).

For all the modeled systems, RDFs were collected over 600 ps-long trajectories. We discuss here the results for model **(b)**, *i.e.*, for the polymer chain with 50 monomer units adsorbed on the CNT with index $n(i) = 10$. Fig. 7 (right) shows the plot of the different RDFs calculated for that model system. The onset of the RDF curves gives a statistical measure of the shortest distance between the CNT and the considered atoms. The RDF between CNT and hydrogen atoms is the first to start deviating from zero, indicating that the atoms closest to the CNT are hydrogen atoms. This means the polymer is mainly interacting with the CNT *via* CH-π interactions. A bit farther, the RDF between CNT and the oxygen atom of the carbonyl group starts to increase: this (as confirmed by the MD trajectory) indicates that most of the carbonyl groups in the polymer are pointing towards the CNT surface. Interestingly, the two types of methyl groups in the repetitive unit have their shortest distance to the CNT wall at the same value: this observation as well as the height of the two corresponding RDFs suggests that both types of methyl groups are adsorbed on the CNT. The RDF analysis therefore indicates there is not a unique (or most favorable) site on the DMAEMA units responsible for the adsorption on the nanotube surface: they can adsorb *via* atoms in both the R1 and R2 groups. The MD trajectory reveals that conformational defects, which can be called as zig-zag-like defects along the

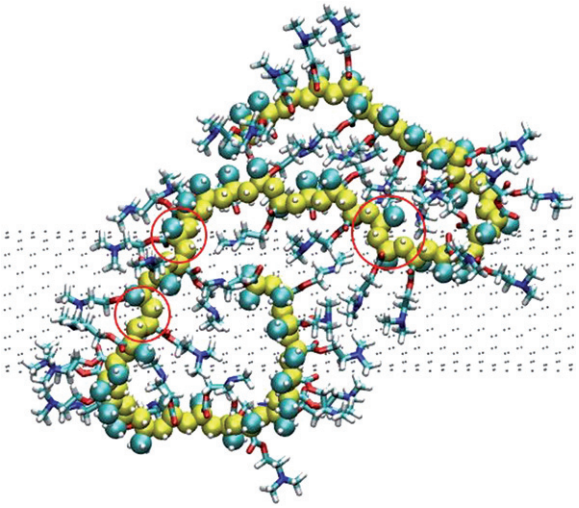

Fig. 8 Top view of a PDMAEMA polymer adsorbed on CNT (model **(b)**). The atoms in the polymer backbone are shown in yellow, the backbone methyl group (group R1) are shown in cyan, while atoms in the R2 groups are sketched with a stick representation. The CNT has been dotted for the sake of clarity. The red circles show conformational defects in the zig-zag polymer chains that cause adjacent monomer units to have different groups adsorbed on the CNT surface.

backbone, can trigger the adsorption of the monomer units with one group or the other.[15] Fig. 8 shows a top view of the adsorbed polymer chain: the red circles highlight some examples of conformational defects in the backbone (depicted in yellow), which result in the adsorption of the different groups. In some cases, due to the high flexibility of R2, both the backbone methyl groups and the methyl substituents of the amine function of a given monomer unit can be adsorbed at the same time. We have observed the same trends for all three models of the PDMAEMA/CNT complex.

In principle, the diversity in the local conformation of the polymer chain backbone, with the presence of *cis*/*trans* defects, could explain the ^{1}H NMR spectrum of the PDMAEMA/CNT complex. However, the segments of the chain adsorbed on the CNT surface may not contribute to the NMR signal, because of the loss of mobility of the adsorbed atoms. While "conformational defects" are present in all the models considered, a peculiar characteristic of the models with long polymer chains (models **(b)** and **(c)**), which are closer to the real system, is the formation of loops. In the loops, the polymer backbone is not in close contact with the CNT, as indicated in Fig. 9 (left) for model **(b)**. Interestingly, the formation of loops seems to be triggered by the presence of so-called zig-zag defects in the polymer backbone. Since in the loops the mobility of the atoms is larger than for those adsorbed on the CNT, they should give a stronger NMR signals. Therefore the conformation adopted by the polymer chain in the loops could be strongly represented in the NMR spectrum of the PDMAEMA/CNT complex. The MD simulations show that in the loops the polymer chain mainly adopts conformations that cause the backbone methyl groups in neighboring monomer units to lie on the same side of the chain, as highlighted by the red ovals in Fig. 9 (right). As a result, those methyl groups are in a chemical environment similar to that in mm triads, which could explain the increased signal at 1.24ppm

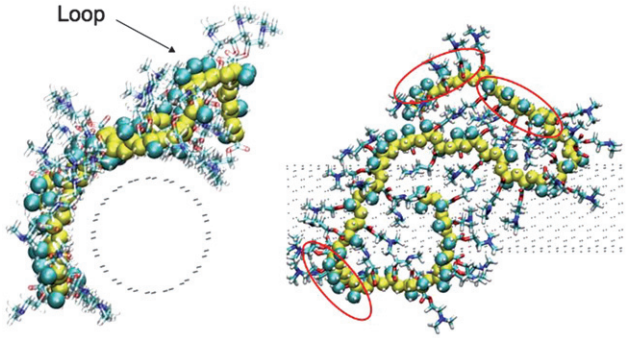

Fig. 9 (left) Front view of a PDMAEMA chain wrapped around a CNT (model **(b)**). The atoms in the polymer backbone are shown in yellow, the backbone methyl groups are shown in cyan, while the rest of the polymer is drawn with a stick representation. The CNT has been dotted for the sake of clarity. A large loop is visible in the upper right part, where the polymer backbone is not in contact with the CNT wall. (right) Top view, with red ovals to highlight parts of the loops where adjacent monomer units adopt conformations that resemble mm triads.

in the ^{1}H NMR spectrum for the PDMAEMA/CNT complex. It is worthy to notice that preliminary simulations on atactic chains of PDMAEMA indicate that the conformational aspects discussed here for the isotactic chains also apply to the atactic ones.

The next part of this work deals with the CNTs dispersion mediated by a poly(L-lactide)-*b*-poly(*N*,*N*-dimethylamino-2-ethyl methacrylate) block copolymer (PLLA-*b*-PDMAEMA) **4**. In this strategy, the PDMAEMA block was expected to anchor onto the CNTs, and in this way, to overcome the inability of the PLA segment to interact with the unsaturated surface of CNTs.

The preparation of the diblock copolymer **4** was performed based on a recently reported procedure.[11] The ring opening polymerization (ROP) of L-lactide with 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) as catalyst, yielded the PLLA **5** with a molecular weight of 9800 g mol^{-1} and a PDI of 1.15 (see Experimental). The derivatization of PLLA block **5** into an ω-bromo PLLA ATRP macroinitiator (PLLA-Br **6**) was then performed by an esterification reaction with α-bromoisobutyryl bromide in chloroform in presence of triethylamine. The formation of the PLLA-Br **6** was fully confirmed by the presence of new resonance signals at 1.98 ppm assigned to the methyl substituents of the bromoisobutyryl end-group. Finally, the PLLA-Br macroinitiator **6** was converted into PLLA-*b*-PDMAEMA diblock **4** by ATRP polymerization of DMAEMA. The molecular weight determination was carried out through ^{1}H NMR spectroscopy and based on the M_n of PLLA-Br (9800 g mol^{-1}). A ratio 1 : 0.4 (L-lactic:DMAEMA units) was found by integration of the respective parts, which corresponded to a molecular weight of about 18200 g mol^{-1} for diblock **4** (Fig. 10).

The GPC analysis of the diblock copolymer shows complete shift of the starting PLA macroinitiator elution peak to lower elution volume, with a PDI of 1.36.

Finally, the PLLA-*b*-PDMAEMA diblock copolymer **4** has been investigated for dispersing the CNTs in THF and chloroform using the conditions previously reported for PDMAEMA **1** homopolymers.

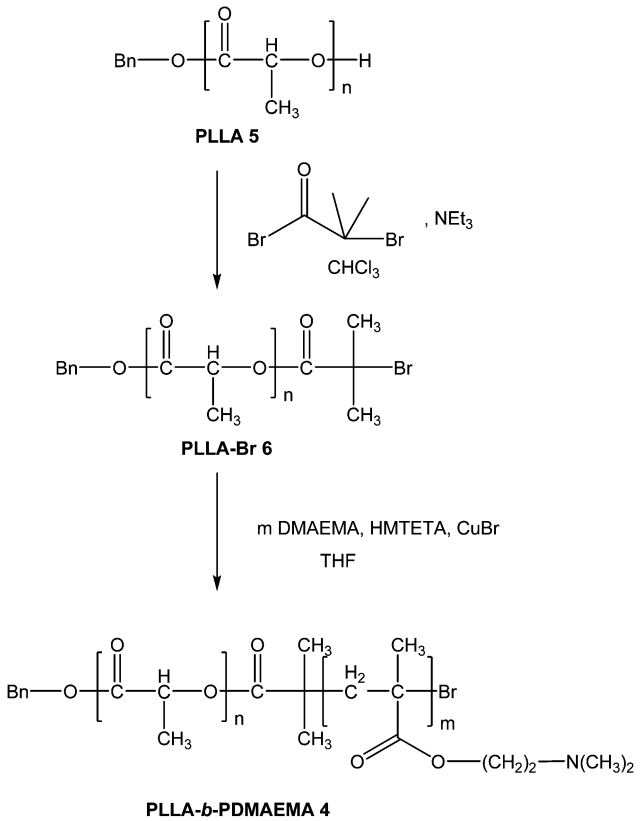

Fig. 10 Synthesis of PLLA-*b*-PDMAEMA diblock **4** from PLLA **5**.

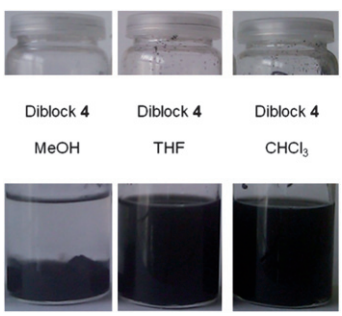

Fig. 11 CNTs dispersion test with PLLA-*b*-PDMAEMA **4** in MeOH (left), THF (centre) and $CHCl_3$ (right).

Interestingly, the samples appeared totally black after treatment, consistent with the issues described with PDMAEMA **1** (Fig. 11). The chloroform solution is allowed being filtered and studied by TEM analysis. Again, very high dispersing capability toward CNTs was observed (not shown here).

The TGA analysis confirms that the polymer **4** as efficient CNT linker is able to strip off CNTs in the chloroform solution after filtration. The residual weight determined at 500 °C has shown unequivocally a certain amount of CNTs (Fig. 12). As expected, in methanol (actually a non-solvent for PLLA), nanotube sedimentation took place leading to transparent and uncolored solution (Fig. 11).

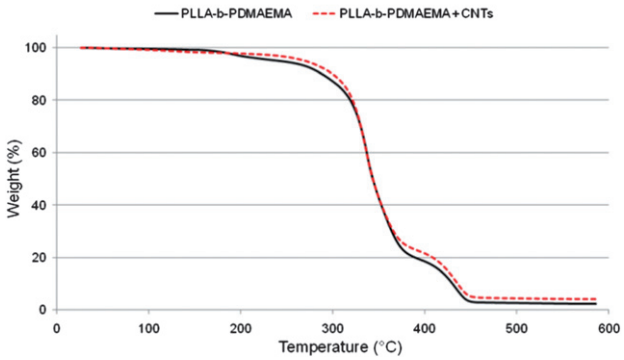

Fig. 12 TGA of PLLA-*b*-PDMAEMA **4** (bold line) and PLLA-*b*-PDMAEMA/CNTs (dotted line).

Conclusion

In summary, this work relied upon CNTs dispersion in organic and aqueous media *via* non-covalent interactions. PDMAEMA demonstrated an unprecedented dispersing ability of CNTs under neutral or ionic form. In water, we observed a high-ratio of nanotube dispersion when PDMAEMA was used under ionic species, namely hydrochloride and quaternary ammonium salts. The same properties were also shown with neutral PDMAEMA in organic solvents.

The mode of interaction between the PDMAEMA and the CNTs was studied by force field-based molecular modeling. In contrast with typical charge transfer from a primary amine towards CNT surface, theoretical experiments have confirmed a specific character of interaction, namely a CH$\cdots\pi$ type interaction involving methyl groups pending along the polyacrylic backbone and substituting to amine functions.

This same binding capability was described with a PLLA-*b*-PDMAEMA block copolymer, the PDMAEMA acting as a linker towards CNTs. In our investigation regarding the formation of CNT-based biomaterials, this strategy appears as a reliable approach for the association of bio-sourced/biodegradable polyesters to carbon nanotubes used as reinforcement agents.

Experimental

Materials

Multi wall carbon nanotubes (MWCNTs) are Grade 7000 from Nanocyl (Belgium). 2-(*N*,*N*-dimethylamino) ethyl methacrylate (DMAEMA) was purchased from Aldrich and filtered through aluminium oxide before use. Hexamethylenetetramine (HMTETA), ethyl α-bromoisobutyrate, α-bromoisobutyryl bromide, copper(I) bromide (CuBr) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Aldrich. DBU was distilled over barium oxide before use. THF was purchased from VWR and filtered through aluminium oxide before use. L-lactide was gifted by Purac.

Instrumental

Gel permeation chromatography (GPC) was performed in THF + 2 wt% NEt_3 at 35 °C using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an

isocratic HPLC pump LC 1120 (flow rate = 1 mL min^{-1}), a Marathon autosampler (loop volume = 200 μL, solution conc. = 1 mg mL^{-1}), a PLDRI refractive index detector and three columns: a PL gel 10 μm guard column and two PL gel Mixed-B 10 μm columns. Poly(methyl methacrylate) and polystyrene standards were used for calibration. Centrifugations were made with a HETTICH Universal 16 Centrifuge. ^{1}H NMR spectra were recorded at ambient temperature with Bruker DPX250 and AMX300 spectrometers. Transmission electron microscopy (TEM) was performed with a Philips CM200 with an acceleration voltage of 200 kV. Thermal gravimetric analyses (TGA) were recorded on a TA Instrument Q500 purged with air. The OPLSAA force field was used, since it is known to provide a reliable description of CH-π interactions, which are likely to take place between the polymer and the CNT surface.[16] All the MD simulations were conducted in the NVT ensemble at room temperature, using the molecular modelling package TINKER.[17] The Andersen thermostat, with a coupling constant of 0.1 ps, was used to maintain the temperature constant. A general cut-off was set to 15 Å for all intermolecular interactions. To save computational time, the geometry of the nanotube was frozen. The rattle algorithm was used to constrain all the C–H bond lengths to their OPLSAA equilibrium value, which allowed setting the time step to 2 fs. MD trajectories were built by recording a snapshot of the systems every 0.5 ps and statistics were performed on 600 ps-long trajectories after equilibrating the system. Different starting geometries were also considered.

Synthesis of poly(*N*-(2-(dimethylamino) ethyl)-methacrylate) (PDMAEMA) 1

DMAEMA (10 g, 63.7 mmol), HMTETA (575 mg, 2.5 mmol) and ethyl α-bromoisobutyrate (244 mg, 1.25 mmol) stirred in 22 mL THF at room temperature for 10 min. Then, the solution was added to CuBr (180 mg, 1.25 mmol) and the resulting mixture heated at 60 °C for 6 h. The green solution obtained was poured on heptane, the solvent removed and the residue solubilized in THF and filtered through aluminium oxide. Yield = 70%.

^{1}H NMR ($CDCl_3$): δ 4.01 (OCH_2), 2.52 (NCH_2), 2.24 (NCH_3), 2.10–1.70 (C–CH_2), 1.30–0.80 (C–CH_3).

M_n determined by GPC (relative PMMA calibration) = 11500 g mol^{-1}, PDI = 1.40.

Synthesis of poly[2-(methacryloyloxy)ethyl] trimethylammonium iodide (PMETAI) 2

PDMAEMA **1** (1 g, 8.6 10^{-2} mmol) and methyl iodide (0.8 mL, 12.3 mmol) were stirred in 10 mL of chloroform for 24 h. Ether was then added and a white powder obtained filtered off. The compound was recovered in pure form quantitatively.

^{1}H NMR (D_2O): δ 4.52 (OCH_2), 3.88 (NCH_2), 3.31 (NCH_3), 2.05 (C–CH_2), 1.10 (C–CH_3).

Synthesis of poly(*N*-(2-(dimethylamino) ethyl)-methacrylate) hydrochloride (PDMAEMA.HCl) 3

Sulfuric acid (98%) was added to a mixture of NaCl in chloroform. The resulting hydrochloride solution was subsequently added to a solution of PDMAEMA **1** in chloroform. After precipitation, the PDMAEMA.HCl was filtered off, washed with ether and dried at 50 °C for 24 h.

^{1}H NMR (CD_3OD): δ 4.39 (OCH_2), 3.61 (NCH_2), 3.05 (NCH_3), 2.05 (C–CH_2), 1.10 (C–CH_3).

Typical procedure for the preparation of MWCNTs dispersion with PDMAEMA 1, PDMAEMA.HCl 3 and PMETAI 2 in water and organic solvents

100 mg of PDMAEMA **1** and 5 mg of MWCNTs were stirred in 10 mL of water overnight. Then, the mixture was centrifugated at 4000 rpm for 10 min.

The solution was adjusted at pH 11 by the addition of saturated sodium carbonate; acidification was carried out with concentrated HCl.

Synthesis of poly(L-lactide) (PLLA) 5

L-lactide (7.81 g, 54.2 mmol) and benzyl alcohol (0.08 mL, 0.77 mmol) were stirred in 50 mL of chloroform. Then, DBU (0.115 mL, 0.77 mmol) was added and the solution stirred at room temperature for 1 h. Three drops of acetic acid were then added and the PLLA precipitated out in hexane. After filtration, the white powder was dried at 70 °C under vacuum overnight. Yield = 85%. M_n determined by ^{1}H NMR = 9800 g mol^{-1}, PDI = 1.15 as determined by GPC (universal calibration).

^{1}H NMR ($CDCl_3$): δ 7.34 (CH arom.), 5.15 (q, J = 7.1 Hz, CH), 1.57 (d, J = 7.1 Hz, CH_3).

Synthesis of α-isopropyloxy, ω-bromoisobutyrate polylactide (PLLA-Br) 6

PLLA **5** (2 g, 0.19 mmol) and triethylamine (0.93 mL, 6.73 mmol) were stirred in 15 mL of chloroform at 0 °C for 20 min. α-Bromoisobutyryl bromide (0.83 mL, 6.73 mmol) was added dropwise and the mixture stirred overnight at room temperature. A small amount of charcoal was then added and the solution stirred for additional 4 h at room temperature. After filtration of charcoal, the PLLA-Br 6 was precipitated in cold methanol, filtered and dried at 40 °C. Yield = 90%.

M_n determined by GPC (universal calibration) = 9800 g mol^{-1}, PDI = 1.41

^{1}H NMR ($CDCl_3$): δ 7.34 (CH arom.), 5.15 (q, J = 7.1 Hz, CH), 1.98 (C(Br)-$(CH_3)_2$), 1.57 (d, J = 7.1 Hz, CH_3).

Synthesis of poly(L-lactide)-*b*-poly(*N*,*N*-dimethylamino-2-ethyl methacrylate) (PLLA-*b*-PDMAEMA) 4

DMAEMA (1.02 g, 6.53 mmol), HMTETA (47 mg, 0.2 mmol) and PLLA-Br **6** (1 g, 0.10 mmol) were stirred in 7 mL of THF at room temperature for 10 min. Then, the solution was added to CuBr (15 mg, 0.10 mmol) and the resulting mixture heated at 60 °C for 20 h. The green solution was then poured on heptane, the powder filtered off and solubilized in dichloromethane. The solution was filtered through aluminium oxide and concentrated. A further precipitation in hexane leads to 1.7 g of product.

M_n determined by GPC (relative PS calibration) = 21500 g mol^{-1}, PDI = 1.36

M_n determined by GPC (relative PMMA calibration) = 24300 g mol^{-1}, PDI = 1.36

M_n determined by ^1H NMR = 18200 g mol^{-1}

^1H NMR ($CDCl_3$): δ 7.31 (CH arom.), 5.13 (CH), 4.02 (OCH_2), 2.53 (NCH_2), 2.25 (NCH_3), 2.10–1.70 (C–CH_2), 1.57 (CH_3), 1.30–0.80 (C–CH_3).

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