Imidazolium end-functionalized poly(L-lactide) for efficient carbon nanotube dispersion†

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Poly(L-lactide) end-functionalized by an imidazolium ring was synthesized by ring-opening polymerization of L-lactide from a hydroxylated ionic liquid. When challenged with CNTs in solution, this polyester exhibited significant binding ability towards the nanotube surface with respect to ω-pyrene poly(L-lactide).

Carbon nanotubes (CNTs) have arisen as novel manufactured nanomaterials with widespread applications in polymeric nanocomposites. This expanding interest relies on their unique structural, physical and mechanical properties, leading to remarkable technological and scientific advances in the development of CNT-based nanostructured compounds.[1] Nonetheless, these nano-objects exhibit a marginal solubility in any solvent due to strong intermolecular π–π interactions. This leads to their bundle arrangement, representing a major drawback for the processability of CNTs. To overcome this issue, covalent and non-covalent functionalizations are usually carried out for the dispersion and the individualization of CNTs within polymeric matrices. Interestingly, the non-covalent, *i.e.*, supramolecular, pathway brings out a simple and cost-effective process supplemented by the entire preservation of the electronic structure of CNTs.[2,3]

Recently, ionic liquids (ILs) have gained tremendous interest due to their versatile physical properties such as chemical and thermal stability, high ionic conductivity, non-volatility and non-flammability, paving the way to a large range of applications like, *e.g.*, low-environmental impact reflective materials.[4] In the field of polymer chemistry, ionic liquids have proved quite versatile for enabling reactions,[5] and substantial efforts have contributed to expand this research in materials science through applications as diverse as liquid crystalline materials, electroactive devices (actuators and sensors) and separation membranes.[6] Another interesting feature of ILs lies in their affinity for the carbon nanotube surface. For instance, imidazolium rings are able to adsorb onto the conjugated π structure due to cation-π and/or π–π interactions, giving rise to CNT bundle disentanglement.[7] This approach has been broadened to polymeric ILs, which afford a good CNT dispersion in aqueous and organic media as a function of the anionic counterion.[8] In this regard, the incorporation of an imidazolium group on polymeric backbones is expected to provide an attractive and efficient strategy aiming at improving CNT interaction and dispersion within polymer matrices. This prompted us to study a new and straightforward approach for anchoring poly(L,L-lactide) (PLLA) chains onto the CNT surface *via* non-covalent (supramolecular) functionalization. Combining bioresorbable PLLA and biocompatible nanoscale-dispersed CNTs[9], this will give access to high-performance CNT-containing biomaterials useful in the biomedical field. Purposely, the formation of PLLA bearing an imidazolium group (ImPLLA **3**) at one chain extremity was performed in $CHCl_3$ at room temperature by ring-opening polymerization (ROP) of L-lactide initiated from a hydroxylated ionic liquid in the presence of 1,8-diazobicyclo[5.4.0] undec-7-ene (DBU) as a metal-free catalyst (Fig. 1). The binding ability of ImPLLA **3** towards the CNTs was evaluated in solution and compared to PLLA end-functionalized by either a pyrene or an anthracene aromatic group, namely PyPLLA **1** and AntPLLA **2**. The functionalization of polymer chains by such polycyclic aromatic moieties is reported as an efficient way to facilitate CNT dispersion in organic media.[10] PyPLLA **1** and AntPLLA **2** were similarly synthesized by ROP of L-lactide using 1-pyrene- and 9-anthracenemethanol, respectively, as initiators. As a first attempt, a set of experiments was carried out with a DBU/alcohol initiator ratio of 0.25/1 and a targeted molecular weight of 10 kg mol^{-1}.

Table 1 shows the molecular characterizations of both PyPLLA **1** and AntPLLA **2** as a function of reaction time.

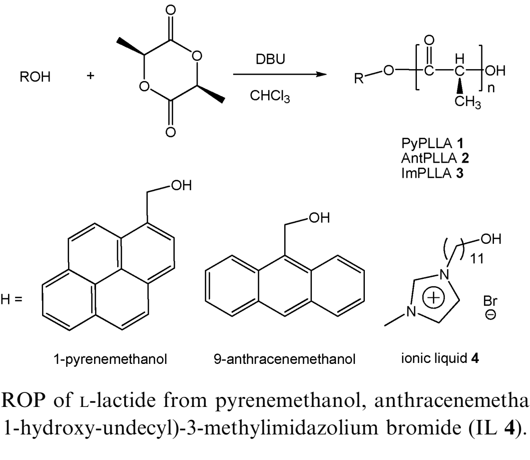

Fig. 1 ROP of L-lactide from pyrenemethanol, anthracenemethanol and 1-(11-hydroxy-undecyl)-3-methylimidazolium bromide (IL **4**).

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Table 1 Molecular characterizations of PyPLLA **1** and AntPLLA **2**

Polymer	Time/min[a]	PDI[b]	$M_n{}^b$/g mol^{-1}	$M_n{}^c$/g mol^{-1}
PyPLLA **1**	10	1.11	9900	—
	20	1.13	10200	—
	30	1.14	10300	9300
AntPLLA **2**	10	1.14	10600	—
	20	1.16	10600	—
	30	1.21	10600	9200

[a] Complete conversion as determined by gravimetry after precipitation into heptane, filtration and drying under vacuum at 70 °C. [b] Determined by SEC in THF at 35 °C using an universal calibration. [c] Determined by MALDI ToF.

In each case, complete monomer consumption was reached after 10 min. Whichever the initiator, a good correlation between theoretical and experimental number-average molecular weights (M_n) together with the exquisite narrow polydispersity index (PDIs) were observed, attesting for the control over ROP of L-lactide.

ROP of L-lactide from 1-(11-hydroxy-undecyl)-3-methylimidazolium bromide **4** was investigated in chloroform with DBU as catalyst under the aforementioned conditions, namely a DBU/IL **4** ratio of 0.25/1, and a targeted molecular weight of ImPLLA **3** fixed to 10 kg mol^{-1} (Fig. 1). It is worth noting that IL **4** functionalized with a hydroxyl group was prepared by quaternization of 1-methylimidazole with 1-bromoundecanol, according to a procedure previously reported in the literature.[11] As far as ROP initiated from 1-(11-hydroxy-undecyl)-3-methylimidazolium bromide **4** is concerned, a slightly faster ROP process is observed with complete monomer conversion reached after only 5 min. Increasing further the reaction time does not show any effect on the evolution of the experimental M_n. However, a dramatic change of associated PDIs is observed as function of time (Table 2).

Broadening of the PDI may have a number of origins such as (i) slow initiation, (ii) chain transfer to monomer, (iii) intra- and/or intermolecular chain transfer and (iv) multiplicity of the active sites (exchanging slowly).[12] Further analyses by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-ToF) were carried out on PyPLLA **1**, AntPLLA **2** and ImPLLA **3**. In the case of polycyclic aromatic-functionalized PLLA, MALDI-ToF analyses corroborate a M_n of 9300 g mol^{-1} for PyPLLA **1** and 9200 g mol^{-1} for AntPLLA **2** in good agreement with both theoretical and experimental (SEC) values. It is worth noting that the control over the ROP is evidenced by a 144 u (atomic mass unit) separation between successive peaks, *i.e.* the molecular weight of lactide unit, attesting to the absence of transesterification process (Fig. 2a). As far as the ImPLLA **3** is concerned, the mass spectrometry analysis obtained after 5 min reveals an increasing amount of transesterified species (Fig. 2b). Even if after 10 min two populations are clearly observed, and in perfect agreement with an exclusive transesterification reaction observed by SEC, a unique repeated peak sequence of 72 u (corresponding to lactic acid residual unit) associated to a very broad PDI, characterizes the sample withdrawn after 20 min (Fig. 2c). The preparation of ImPLLA with higher molecular weight is still under investigation.[13]

Table 2 Molecular characterizations of ImPLLA **3**

Time/min[a]	PDI[b]	$M_n{}^b$/g mol^{-1}	$M_n{}^c$/g mol^{-1}
5	1.18	8500	9500
10	1.32	8500	9600
20	2.02	8500	—

[a] Complete conversion as determined by gravimetry after precipitation into heptane, filtration and drying under vacuum at 70 °C. [b] Determined by SEC in THF at 35 °C using an universal calibration. [c] Determined by MALDI ToF.

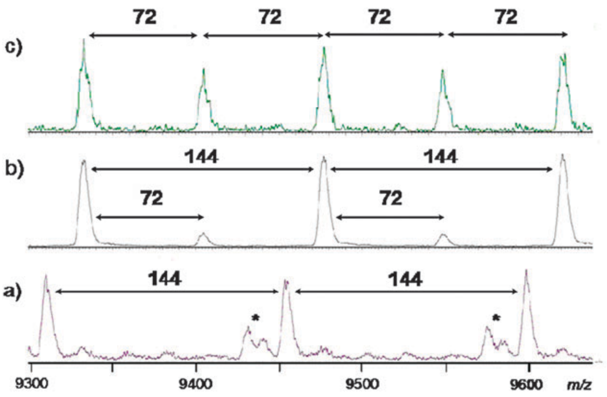

Fig. 2 MALDI ToF spectra of AntPLLA **2** (a) and ImPLLA **3** obtained after 5 (b) and 20 min (c). * refers to the radical cation of the AntPLLA 2.

In order to shed some light on the CNT dispersion ability of end-functionalized PLLA **1–3**, a first visual dispersion test was carried out in $CHCl_3$ using a simple procedure. Three PLLA samples characterized by comparative M_n (*ca.* 9.5 kg mol^{-1}) and narrow PDI were dispersed with CNTs for the same molar quantity of polycyclic aromatic and imidazolium end-groups. A solution of ~100 mg of **1–3** (1.1 × 10^{-5} mol) and 5 mg of CNTs was stirred overnight in 10 mL of chloroform at r.t. After centrifugation at 4000 rpm for 10 min, the resulting mixtures showed dramatic variations of CNT dispersion, without requiring any sonication (Fig. 3).

As far as the AntPLLA **2** is concerned, the solution remained colorless with complete sedimentation of CNTs already after a few seconds. This behaviour was attributed to the weak interaction between the anthracene group and the CNT surface, at least in chloroform. By proceeding with PyPLLA **1**, and even if CNT sedimentation is also quickly observed, the upper solution showed a slightly dark color. This lies in a stronger π–π stacking interaction between the nanotube sidewall and the pyrene end-group of **1** with respect to AntPLLA **2**. Interestingly enough, ImPLLA **3** demonstrated a

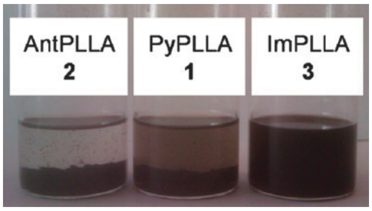

Fig. 3 CNTs dispersion test with polymers **1–3** in chloroform.

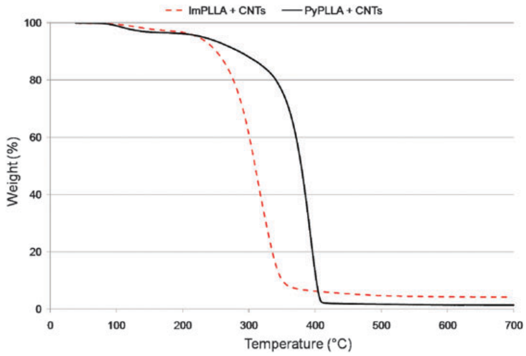

Fig. 4 TGA analyses of PyPLLA **1** and ImPLLA **3** as obtained from a chloroform suspension of CNTs after cotton-filtration and drying under vacuum.

very high binding ability as clearly highlighted by extensive dispersion of CNTs in chloroform. After two days, total CNT sedimentation is observed in presence of PyPLLA **1**, while the solution with ImPLLA **3** revealed a stable behaviour over a period of time as long as two months. The binding affinity of ImPLLA **3** was supported by TGA analyses performed on the supernatant fraction recovered after cotton-filtration and evaporation of $CHCl_3$ from these CNTs dispersion (Fig. 4).

After the complete degradation of PLLA backbones, a residue of *ca.* 5 wt% for CNT-based suspensions derived from ImPLLA **3** was obtained, much higher than the residue recovered with PyPLLA **1** (*ca.* 1 wt%). This trend in terms of residue indicates that ImPLLA **3** is by far more efficient for solubilizing CNTs in $CHCl_3$ through cation–π (in addition to π–π) interactions rather than PyPLLA **1**. Finally, the resulting suspension of CNTs with ImPLLA **3** was used for a transmission electron microscopy (TEM) analysis. After solvent evaporation, a complete dispersion joined to an individualization of CNTs was evidenced. Most CNTs are wrapped with the polymeric chains; the ionic part, particularly bromide ions, was highlighted by the black spots, revealing the presence of ω-imidazolium functionalized PLLA chains clustered around CNTs (Fig. 5).

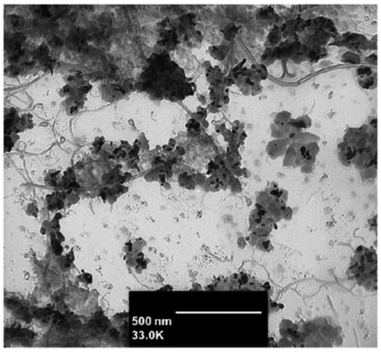

Fig. 5 TEM image obtained, after solvent evaporation, from a chloroform suspension of CNTs with ImPLLA **3**.

In summary, we presented the synthesis and CNT dispersion ability of new poly(L-lactide) incorporating an imidazolium, a polycyclic anthracene or pyrene as end-group. These ω-functionalized polyesters were prepared by metal-free ring-opening polymerization of L-lactide in good yields with good control over their molecular parameters. Subsequently, their ability to interact with the CNTs' surface through cation-π and/or π–π interactions was evaluated in chloroform. Pyrene and imidazolium containing PLLA have demonstrated an unambiguous affinity with the π-conjugated structure owing to the large quantity of solubilized CNTs. However, ImPLLA **3** clearly revealed CNT dispersion ability significantly higher than PyPLLA **1**. The functionalization of polymeric compounds with an imidazolium ring thereby arises as an efficient, rational and reliable strategy to the CNTs dispersion in organic media through non-covalent interactions. These approaches bring new supramolecular tools to the formation of CNT-based biomaterials derived from renewable resources with high performance properties.

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