

# Supramolecular interactions of carbon nanotubes with biosourced polyurethanes from 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-1,3-propanediol

Maurizio Galimberti <sup>a,\*</sup>, Vincenzina Barbera <sup>a</sup>, Attilio Citterio <sup>a</sup>, Roberto Sebastiano <sup>a</sup>, Ada Truscillo <sup>a</sup>, Antonio Marco Valerio <sup>a</sup>, Lucia Conzatti <sup>c</sup>, Raniero Mendichi <sup>b</sup>

<sup>a</sup> Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering "G. Natta", Via Mancinelli 7, 20131 Milano, Italy

<sup>b</sup> National Council of Research, Institute for the Study of Macromolecules, Via Bassini 15, 20133 Milano, Italy

<sup>c</sup> National Council of Research, Institute for the Study of Macromolecules, Via De Marini 6, 16149 Genova, Italy

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## 1. Introduction

The preparation of innovative macromolecular structures from renewable sources is one of the hot research topic in the polymer field [1,2]. Such a research activity becomes particularly meaningful when there is no impact on the food chain, starting building blocks are relatively available and reasonable economic perspective can be envisaged.

Glycerol is a cheap, easily available raw material, non toxic and biodegradable. It is the main co-product of bio-diesel production: some 65% of glycerol came from the biodiesel industry in 2011, with a total supply of 1.2 million ton in 2010 [3–8]. Glycerol is studied as the building block for a C3 platform alternative to the oil based one [3,4,8–10], but is not much used for the preparation of polymers [10], mainly as a consequence of high viscosity and high hydrophilicity and because of the presence of three hydroxyl groups with similar reactivity, that could lead to side products. Hence, alternatives routes that start from simple glycerol derivatives are

preferred. For example, glycerol carbonate is used for the synthesis of polyurethanes, polycarbonates or polyethers [10].

The present work started from 2-amino-1,3-propanediol, known as serinol (**S**), with the objective to prepare innovative polymeric structures and to establish supramolecular interactions with carbon allotropes, exploiting the chemoselectivity of amino and hydroxyl groups. Serinol is commercially available, is prepared from glycerol or dihydroxyacetone, but can also be directly obtained from renewable sources [11].

As first step of the research activity, the reaction of the amino group of **S** with 2,5-hexanedione (**HD**), through the classical Paal–Knorr reaction [12,13], was performed to prepare 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-1,3-propanediol, whose chemical structure is shown in Fig. 1, serinol derivative containing a pyrrole ring, hereinafter indicated as serinol pyrrole (**SP**) [14].

Report on Paal–Knorr reaction between **S** and **HD** is available in the literature. **S** and **HD** were refluxed in toluene in the presence of large amount of glacial acetic acid and of a catalytic amount of *p*-toluenesulfonic acid. **SP** was obtained in low yield, 13 as mol%, together with polymeric products [15]. Objective of the present work was thus to improve, substantially, reaction pathway and efficiency, performing the neat reaction of **S** with **HD**. **SP** shows what could be defined a dual reactivity. Thanks to the hydroxyl

\* Corresponding author.

E-mail address: maurizio.galimberti@polimi.it (M. Galimberti).

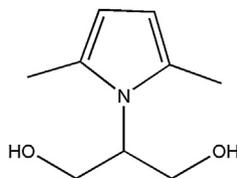


Fig. 1. 2-(2,5-dimethyl-1H-pyrrol-1-yl)-1,3-propanediol (**SP**).

groups, it appears suitable monomer for stepwise polymerizations. Moreover, the pyrrole ring could be exploited for establishing supramolecular interactions that involve  $\pi$  electrons.

Stepwise polymerizations were performed [16]. Those to poly(ether)s, poly(ester)s, poly(carbonate)s and poly(urethane)s are still under investigation. In this manuscript, are described poly(urethane)s (PU) prepared from **SP** and 1,6-hexamethylene diisocyanate (**HDI**), through a solvent free synthesis. In the literature, the use of serinol for polymers preparation is not yet carefully investigated. Only a couple of examples have been reported in recent papers. The reaction of the amino group of serinol with electrophiles led to functional diol intermediates, that cyclized to form six-membered aliphatic cyclic carbonate monomers, converted into polymers through organo-catalysed ring opening polymerization [17]. In another report [18], water soluble biodegradable polyester for selective drug release was prepared from adipoyl chloride and a serinol derivative obtained from the reaction of serinol with succinimidyl ester of trimethyl-locked benzoquinone. Characterization of PU prepared in this work was performed by means of Fourier Transformed Attenuated Total Reflectance (FT-ATR),  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, gel permeation chromatography (GPC), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC).

PU based on **SP** were then used to establish supramolecular interaction with Multiwalled Carbon Nanotubes (MWCNT) [19], exploiting the synergy between pyrrole and carbonyl  $\pi$  systems of PU for establishing effective interaction with CNT. In fact, particular objective of the research was to establish stable supramolecular interactions with carbon nanotubes, that could allow the preparation of stable dispersions in liquid media and of composite materials with carbon nanotubes tightly bound to the polymer matrix, preventing their dispersion in the environment. MWCNT are concentric tubes of graphene sheets, with nanosize in two dimensions, characterized by exceptional mechanical properties and with the ability of conducting electrons without dissipating energy as heat. Despite the impressive research activity on both single- [20,21] and multi-walled [22,23] CNT, efficient approaches to convert CNT bundles into fully dispersed nanometric CNT having a stable interaction with the matrix, remain a main research objective. Main concern that limits the large scale use of MWCNT is indeed their dispersion in the environment, as a consequence of faint interaction with their surrounding. To promote such interaction, reviews are available in the scientific literature on carbon nanotubes, reporting their covalent chemical modification [24–27] and non-covalent interactions [27]. The latter ones do not alter the electronic structure of nanotubes, thus preserving their exceptional properties. Among them, polynuclear aromatic compounds carrying different substituents and polymers with aromatic structural units are reported to promote the solubility of CNT in hydrophilic or hydrophobic media. Stable dispersions of MWCNT in toluene, tetrahydrofuran and chloroform were prepared thanks to copolymers of methyl methacrylate bearing as pendant pyrene groups randomly distributed along the chains [28,29]. Styrene based copolymers with a pyrene block were then shown to improve

the solubility of SWCNT in tetrahydrofuran [30] and stable solutions of SWCNT and MWCNT in tetrahydrofuran were obtained with aliphatic polyester dendrons bearing pyrene units at their periphery [31]. A pyrene functionalized RAFT agent was used to synthesize pyrene functionalized polymers that promoted the preparation of stable solutions of MWCNT in tetrahydrofuran [32].

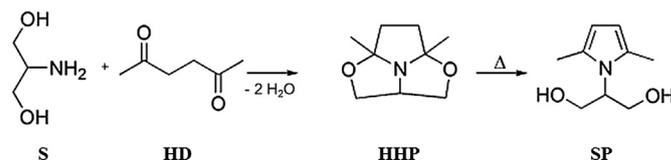
CNT were functionalized with a poly(benzoxazole) (PBO) precursor [33], enabling the CNT dispersion in dimethylacetamide. Afterwards, a CNT-PBO adduct film with improved mechanical properties was obtained by simple heating. Moreover, stable concentrated dispersions of MWCNT and single-walled CNT in THF and toluene were prepared by using poly(2,7-carbazole)s [34] and poly(phenylacetylene)s with long alkyl tails on the side-chains [35]. In all cases, the absence of hydrophilic moieties allows the dispersion of CNT only in aromatic solvents. The use of **SP** as monomer could allow the preparation of polymers with tuned amounts of aromatic rings in the backbone chain and with hydrophilic moieties that could favour the CNT dispersion in aqueous and environmentally friendly media. The structure of MWCNT-PU adducts was characterized through High Resolution Transmission Electron Microscopy (HRTEM) and the stability of MWCNT-PU suspensions in eco-friendly solvents, such as acetone and ethyl acetate, was investigated. Preliminary results arising from centrifugation technique and UV spectroscopy are also reported.

## 2. Results and discussion

### 2.1. Synthesis of 2-(2,5-dimethyl-1H-pyrrol-1-yl)-1,3-propanediol

The serinol derivative 2-(2,5-dimethyl-1H-pyrrol-1-yl)-1,3-propanediol was prepared by condensation of **S** and **HD** through the classical Knorr–Paal synthesis of pyrroles. As depicted in Scheme 1, two-step synthesis was developed.

The neat reaction of equimolar amounts of **S** and **HD** was first performed, at room temperature, obtaining the tricyclic compound 4a,6a-dimethyl-hexahydro-1,4-dioxo-6b-azacyclopenta[cd]pentalene (**HHP**), that was then isomerized to aromatic **SP** by simply increasing the reaction temperature. Both reactions were thus performed in the absence of solvents and catalysts. Quantitative yield was obtained for the first step reaction and, after distillation of **SP**, the overall yield of the two steps synthesis was calculated to be about 95% by moles. Structural characterizations of tricyclic compound and **SP** was performed by means of  $^1\text{H}$  NMR. It is worth commenting here that the NMR spectra of the reaction mixtures did not reveal the presence of products other than **HHP**, after the first step, and **SP**, after the second step. Research is in progress to further optimize reaction conditions and yields and to elucidate the mechanism. At present, as far as the first step of the synthesis is concerned, it can be commented that the absence of acids and the mild reaction conditions favour hemiaminal formation and polycyclization and prevent the aromatization to **SP** as well as the formation of polymeric products. Water, that was not removed from the products of the first step, could favour such isomerization, bringing acidity, as a consequence of temperature increase, at a level however not enough to promote the polycondensation process.



Scheme 1. Reaction scheme for the preparation of the serinol derivatives **HHP** and **SP**.



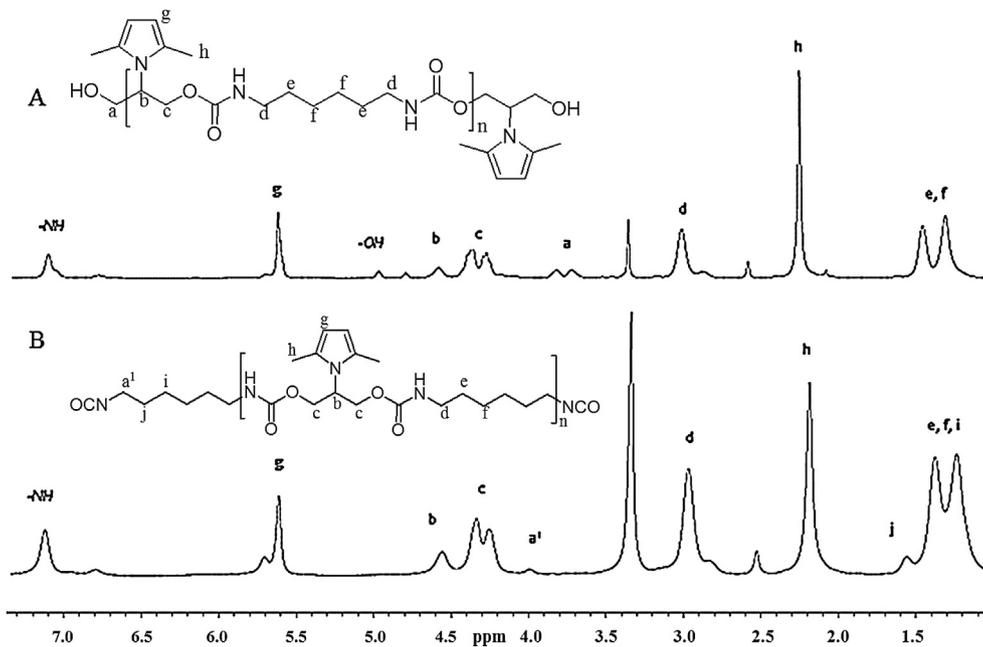


Fig. 3. Structure and  $^1\text{H}$  NMR spectra 400 MHz in  $\text{DMSO-d}_6$  of sample from Entry 4b (A) and from Entry 5b (B) of Table 1.

to the carbamate N–H, is typical of urethane linkage. Methylene protons (c) of the repeating serinol unit produce signals at 4.30 and 4.21 ppm. Peaks at 4.53 and at 2.94 ppm represent the resonance respectively of the methine hydrogen (b) and of the methylene ones (d) bonded to carbamate N–H. Absorptions at 3.76 and 3.66 ppm indicate the presence of  $\text{CH}_2\text{OH}$  terminals (a, Fig. 3A), and the one at 3.96 ppm is attributed to the hydrogens on the C carrying the terminal isocyanate ( $\text{a}^1$ , Fig. 3B). Both spectra also show the characteristic signals of the heterocyclic unit: at 5.59 ppm, the pyrrolic hydrogens in the  $\beta$ -position, and at 2.17 ppm the methyl group in  $\alpha$ -position.

$^{13}\text{C}$  NMR spectra of the reaction products obtained from Entries 4b and 5b of Table 1 are reported in Fig. 4A and B, respectively.

The presence of urethane carbonyl and aromatic pyrrolic carbons are revealed by peaks at 155, 127 and 106 ppm, respectively. Most noticeable differences between the two samples are visible in the area between 40 ppm and 63 ppm. In Fig. 4A, it is possible to note the presence of the signal of terminal methylene (a) at 61 ppm.

Instead, in the same area of the spectrum shown in Fig. 4B, the signal at 42 ppm ( $\text{a}^1$ ) is relative to the methylene carbon adjacent to the isocyanate nitrogen.

Thermal stability of **SP**-based oligomers was assessed by means of thermal gravimetric analysis (TGA) under  $\text{N}_2$ . As an example, TGA scans of **SP** and of the PU sample obtained from Entry 4b of Table 1, with hydroxyl end groups, are compared in Fig. 5.

Weight loss for the sample from Entry 4b in the temperature range 25–150  $^\circ\text{C}$  is likely due to evolution of adsorbed water. The onset temperature for the degradation of the pyrrole based unit in the oligomeric product can be detected around 300  $^\circ\text{C}$ . No comparison is possible with **SP**, that achieves at lower temperature its boiling point. Further weight losses are observed at about 350  $^\circ\text{C}$  and 385  $^\circ\text{C}$  and are due to the degradation of carbamate linkage and to the methylene sequences [36].

The presence of thermal transitions was investigated through DSC analysis. Glass transition was observed at about 17  $^\circ\text{C}$  and 13  $^\circ\text{C}$  respectively, for PU samples from Entries 4b and 5b of Table 1, with

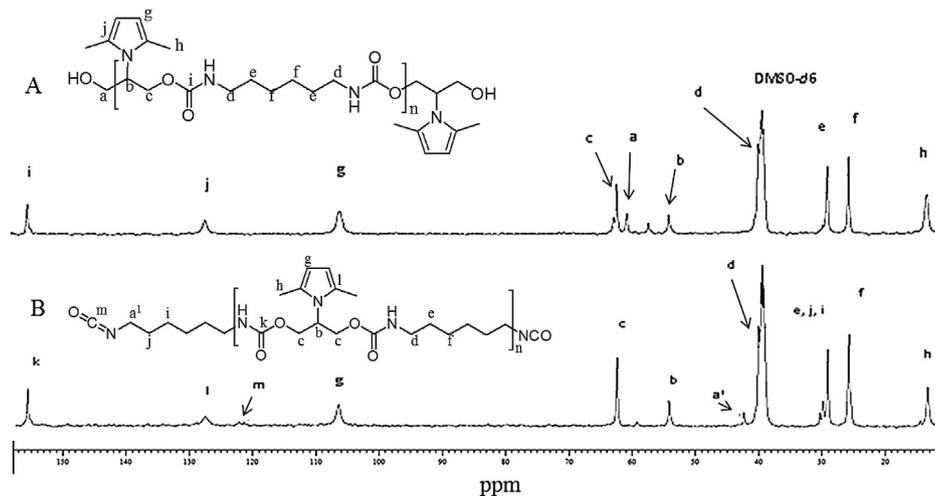


Fig. 4. Structure and  $^{13}\text{C}$  NMR spectra 100 MHz in  $\text{DMSO-d}_6$  of PU samples from Entry 4b (A) and from Entry 5b (B) of Table 1.

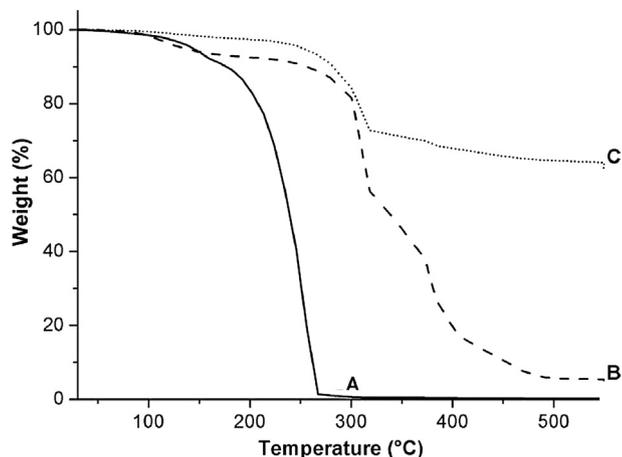


Fig. 5. TGA curves under  $N_2$  of SP (A), PU (B), PU-MWCNT adduct (C), with PU sample from Entry 4b of Table 1.

hydroxyl and isocyanate end groups respectively. The sample with 2,2-dimethyl-1,3-propanediol as the diol (Entry 7b of Table 1) showed glass transition at about 10 °C. These values, clearly affected by the low molecular mass of the oligomers, could however indicate that SP-based repeating unit lead to higher temperatures for the glass transition.

### 2.3. Adducts of poly(urethane)s based on SP with MWCNT

Adducts of poly(urethane)s based on SP with MWCNT were prepared, in order to obtain stable dispersions of disentangled nanotubes in eco-friendly polar solvents, suitable for large scale applications, such as those for coatings. The Paal–Knorr reaction transforms the  $sp^3$  hybrids of the amino group in the  $sp^2$  ones of the pyrrole ring. This allows to pursue the  $\pi$ - $\pi$  interaction with the  $sp^2$  hybridized carbon atoms of CNT.

PU adducts with MWCNT were prepared as described in the experimental part. Briefly, an acetone solution of a PU sample from one of the Entries of Table 1 was added to a sonicated CNT suspension in acetone, performing then a further sonication. The concentration adopted for the MWCNT/PU adduct was 1 mg/mL. Chemical composition and structure of the ensuing MWCNT-PU adduct were investigated by means of TGA, XRD and HRTEM analysis. The sample analysed was isolated by carefully taking the upper part of the supernatant suspension obtained after centrifugation, evaporating then the solvent. By using the PU sample from Entry 3 of Table 1, the content of PU was calculated, from TGA, to be about 46 as mass% (Fig. 5A). Fig. 6 shows the XRD patterns, in the  $10^\circ$ – $100^\circ$  as  $2\theta$  range, of pristine MWCNT (Fig. 6A) and of the MWCNT-PU adduct (Fig. 6B) with PU from Entry 3 in Table 1. XRD pattern of a crystalline carbon allotrope, such as graphite, that has many stacked graphene layers, shows, as the most intense peaks, some (00 $l$ ) and (hkl) reflections, that remain visible also when the number of stacked layers is reduced (to few tenths) [37]: 002 and 004, at  $26.2^\circ$  and  $54.3^\circ$  as  $2\theta$  value, with a  $d_{002}$  interlayer distance of 0.34 nm, 100 and 110 reflections at  $42.8^\circ$  and  $77.5^\circ$  as  $2\theta$  value. In the pattern in Fig. 6A of MWCNT that have a low number of layers wrapped to formed the tubes, only the two most intense reflections are visible: 002 at  $25.3^\circ$  and 100 at  $42.8^\circ$ . The same reflections can be observed in the pattern of the MWCNT-PU adduct. The dimension of crystallites in direction orthogonal to CNT layers can be estimated, by calculating the correlation length  $D_{00l}$ , through the Scherrer equation. A value of about 2.7 nm was obtained for both pristine tubes and for the adduct. Taking into account the distance

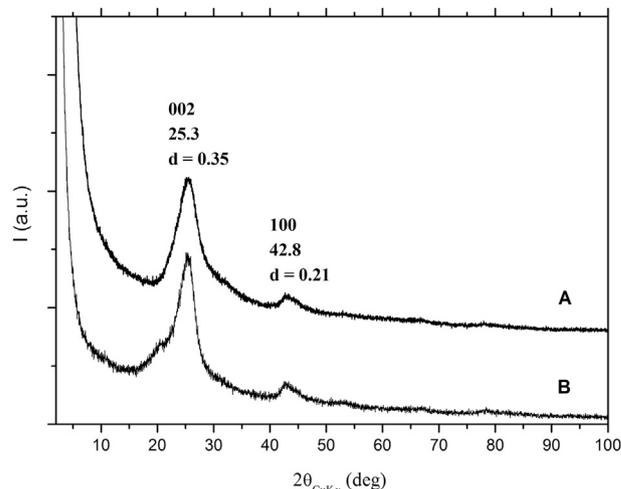


Fig. 6. XRD diffraction spectrum of: MWCNT (A), the MWCNT-PU adduct (B). PU was from Entry 3 of Table 1.

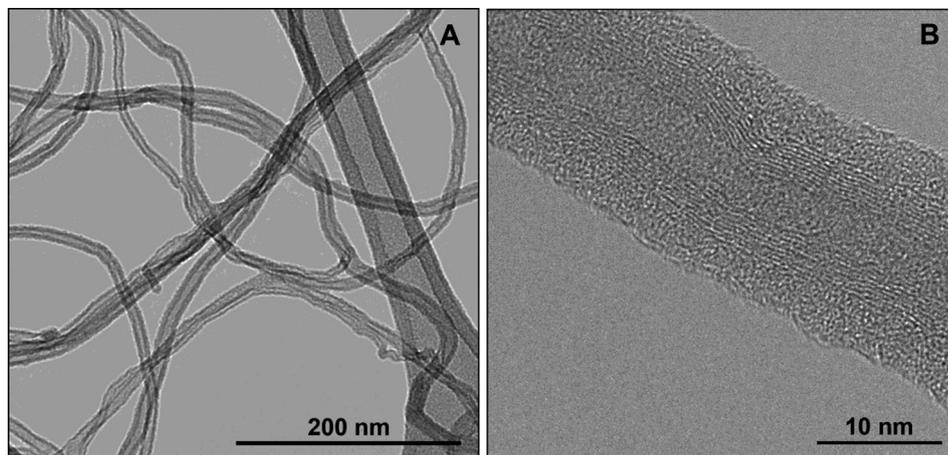
between two successive layers in CNT graphitic crystal, 8 was estimated as the number of wrapped CNT layers.

Morphological analysis of MWCNT and MWCNT-PU adduct was performed through HRTEM analysis at different magnifications. PU treatment brought to a large CNT disentanglement, as shown by the lower number of CNT micrometric bundles and by the presence of individual tubes in a defined space, as observed in many HRTEM images and represented in Fig. 7A. The micrograph in Fig. 7B shows that the multiwalled CNT skeleton remained intact after the treatment with PU oligomers. The inspection of such images allowed to estimate the average number of CNT layers equal to 10, a value close to the one calculated from the XRD pattern. The coherence between the results obtained from XRD and HRTEM indicates that the MWCNT-PU adduct shown in Fig. 7 (CNT with 10 walls) is representative of the whole sample. CNT surface was thus decorated with PU chains, that form condensed polymer layer tightly adhered to the CNT external surface, with a thickness from about 3 to about 9 nm.

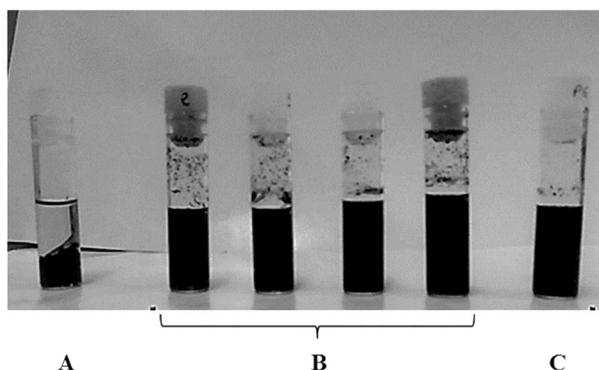
Acetone suspensions of MWCNT-PU adducts (1 mg/mL concentration) were prepared with PU from Entries 2, 3, 4b and 5b of Table 1, with PU content of  $46 \pm 0.5$  as mass% (see Experimental Section). Such suspensions were observed to be stable for at least 12 months. Fig. 8 shows the pictures of the acetone suspensions of MWCNT (Fig. 8A) and of MWCNT-PU adducts after 12 months of storage (Fig. 8B). The stable MWCNT-PU suspension (with PU from Entry 3 of Table 1) was then centrifuged, at 5000 rpm for 5 min, without observing any evident separation, as shown in Fig. 8C.

To confirm the dispersion of the MWCNT-PU in the solvent, UV–Vis absorption analysis was carried out on the suspensions shown in Fig. 8, by carefully taking the upper part of the supernatant suspensions, obtaining the relation between absorbance and MWCNT-PU concentration. Solutions with 0.1, 0.3, 0.5 and 1 mg/mL as adduct concentrations were analyzed. In Fig. 9A, it is shown that the absorbance monotonously increases with the adduct concentration. Moreover, the stability of the solution with 1 mg/mL concentration of the PU/MWCNT adduct, prepared with PU from Entry 3 of Table 1, was investigated by taking UV–Vis spectra after 12 months. In Fig. 9B, it is evident that the same absorbance was detected for the suspensions (1 mg/mL) freshly prepared and stored for 12 months (traces b and c), confirming that CNT treated with PU oligomer did not settle down, even after long time.

To investigate the specific role of the aromatic ring, CNT adduct was as well prepared with PU based on DMP in place of SP (Entry 7



**Fig. 7.** HRTEM micrographs of: individual tubes (A), the MWCNT-PU adduct (PU from Entry 3 of Table 1) (B).



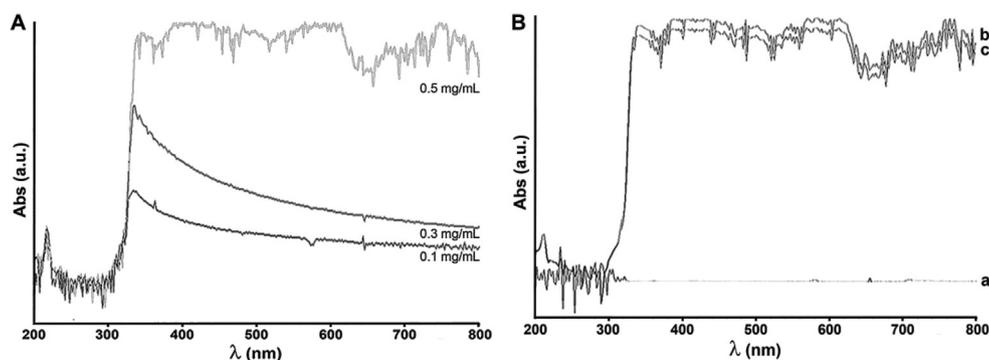
**Fig. 8.** Acetone suspensions of MWCNT (A), MWCNT-PU after 12 months storage (B) and MWCNT-PU after centrifugation (C). In (B), vials from left to right contain PU obtained from Entry 2, 3, 4b, 5b of Table 1, respectively. In (C), vial contains PU from Entry 3 of Table 1.

of Table 1). Extraction tests with ethyl acetate at room temperature were then carried out on both CNT adducts. TGA analysis of the ensuing products showed weight loss of about 23 wt% and 1 wt% for the adduct with PU based on **DMP** and **SP** respectively, revealing the strong supramolecular interaction of PU based on **SP** with CNT. These results are in line with the analysis of TEM micrographs that, as shown in Fig. 7, revealed the intimate interaction of MWCNT with the **SP** based PU. It was thus achieved the objective mentioned

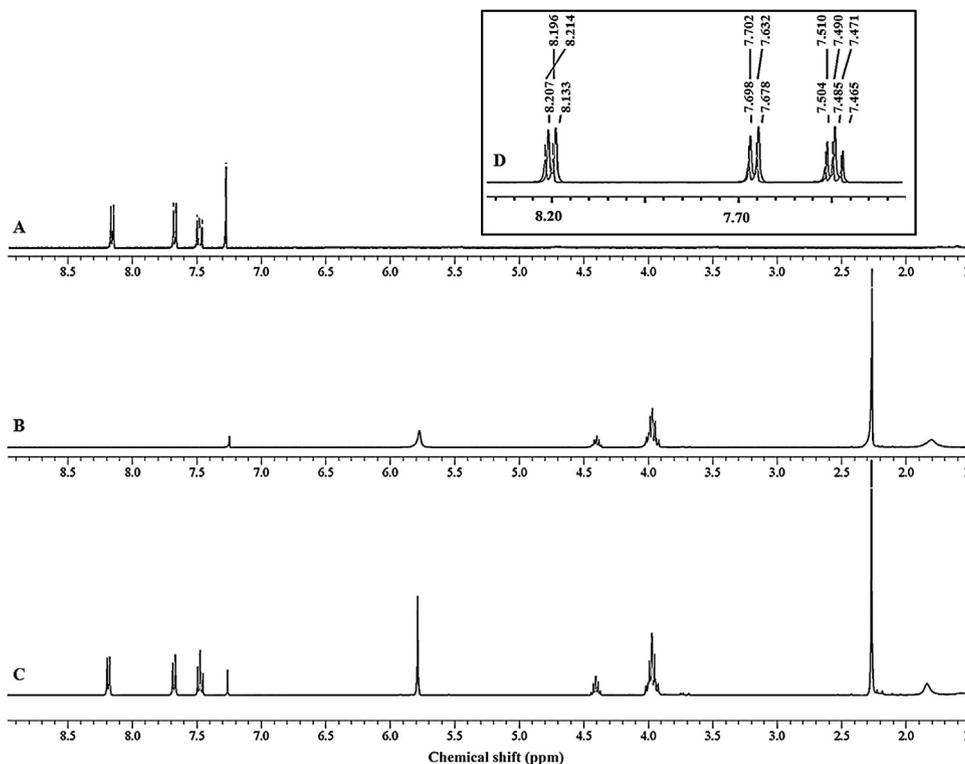
in the introduction, to exploit the synergy between pyrrole and carbonyl  $\pi$  systems for establishing stable interaction with CNT.

#### 2.4. Interaction of SP with CNT

The above reported results suggest that **SP** promote stable interaction of poly(urethane)s with CNT. Experiments were performed to obtain at least a clue on the nature of such interaction. In the literature,  $\pi$ - $\pi$  interactions are hypothesized to occur between aromatic molecule and carbon allotropes [38–41]. To investigate such interaction, polynuclear aromatic molecules, such as pyrene [42], coronene [42] and perylene [43], are used as model compounds, essentially for the aromatic molecules. In this work, to avoid any possible influence from by products present in CNT, such as catalyst residues, perylene was used as model compound for CNT and its interaction with **SP** was studied through NMR analysis. In fact, it was shown that it is possible to obtain a direct evidence for the  $\pi$ - $\pi$  interaction by means of  $^1\text{H}$  NMR spectral measurements [40]. In brief, increasing amounts of perylene were added to a so-lution containing **SP**, recording the NMR spectra. In Fig. 10, are re-ported the  $^1\text{H}$  NMR spectra of perylene (Fig. 10A) **SP** (Fig. 10B) the perylene adduct with **SP** (Fig. 10C). The chemical shifts of the perylene-protons in the serinol pyrrole solution shifted to higher magnetic field by ca. 0.007–0.003 ppm (Fig. 10D), compared to those recorded for the perylene solution. The shift is due to the effect of the electron rich system (pyrrole), in agreement with what reported in the literature. It appears thus that the **SP** molecule is



**Fig. 9.** Dependence of UV-vis absorbance on concentration of PU-MWCNT adduct in acetone (A); UV traces for acetone suspensions of: MWCNT (a), MWCNT-PU adduct (b), MWCNT-PU adduct after twelve months storage (c) (PU from Entry 3 of Table 1) (B).



**Fig. 10.**  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3$  of perylene (A); **SP** (B); Perylene-**SP** adduct (C). Comparison of spectra C and A in the inset D: enlargement between 7.40 and 8.40 ppm.

able to interact with a polynuclear aromatic compound, thanks to its  $\pi$  electrons. However, further investigations are required to be better elucidate the nature of such interaction.

### 3. Conclusion

Innovative, green, efficient synthetic strategy was designed and developed for the preparation of polyurethanes able to establish stable supramolecular interactions with carbon nanotubes. Serinol derivative containing a pyrrole ring, 2-(2,5-dimethyl-1H-pyrrol-1-yl)-1,3-propanediol, was synthesized in a two step reaction involving equimolar amount of serinol and 2,5-hexandione, without the use of solvents and further chemicals. **SP** was obtained from the aromatization of the tricyclic intermediate 4a,6a-dimethyl-hexahydro-1,4-dioxa-6b-azacyclopenta[cd]pentalene, that is the product of the first step of the synthesis. PU oligomers were synthesized through the reaction of **SP** with **HDI** and their adduct with CNT was prepared by sonication in an environmentally friendly solvent such as acetone. Stability of the suspension was verified over months, even after centrifugation. HRTEM analysis revealed that CNT were prevalingly disentangled from the starting bundles. They had intact skeleton and were decorated by PU oligomers, tightly adhered to CNT surface. This work demonstrates that **SP** is a versatile monomer for the preparation of polymers that allow to exploit the  $\pi$ - $\pi$  interaction between the pyrrole ring and a carbon allotrope such as CNT, leading to the preparation of even and stable CNT dispersions in a large variety of environments, from eco-friendly (aqueous) liquids to polymeric matrices. A biosourced molecule such as **SP** can thus pave the way for the preparation of composite materials with carbon allotropes, particularly of nanosize, tightly bound to the polymer matrix, preventing their dispersion in the environment.

The use of MWCNT-PU adducts for the preparation of PU based nanocomposites is currently under investigation.

## 4. Experimental section

### 4.1. Materials

Reagents and solvents commercially available were purchased and used without further purification: 2,5-hexandione (Merck – Schuchardt), 2-amino-1,3-propanediol (kindly provided by Bracco), 1,6-hexamethylene diisocyanate (Fluka – Analytical), perylene (Sigma–Aldrich), 2,2-dimethyl-1-propanol (Fluka – Analytical), acetone (Sigma–Aldrich), ethyl acetate (Sigma–Aldrich). Purified multi-walled nanotubes (NC7000 series) were purchased from NANOCYL™ Inc. They have average length of 1.5  $\mu\text{m}$ , average diameter of 9.5 nm, surface area of 250–300  $\text{m}^2/\text{g}$ , 90% as carbon purity and 10% as metal oxide content.

### 4.2. Synthesis of 4a,6a-dimethyl-hexahydro-1,4-dioxa-6b-azacyclopenta[cd]pentalene (HD)

A mixture of hexan-2,5-dione (41.4 g; 0.36 mol) and serinol (30.0 g; 0.33 mol) was poured into a 100 mL round bottomed flask equipped with magnetic stirrer. The mixture was then stirred, at room temperature, for 6 h. The resulting compound **HD** was characterized through  $^1\text{H}$  NMR and the yield was estimated to be 99%.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ,  $\delta$  in ppm): 1.28 (s, 6H); 1.77 (m, 2H); 1.93 (m, 2H); 3.60 (m, 4H); 3.94 (q, 1H).

### 4.3. Synthesis of 2-(2,5-dimethyl-1H-pyrrol-1-yl)-1,3-propanediol (SP)

The product mixture obtained from the synthesis of **HD** was kept under vacuum for 2 h and then heated to 180  $^\circ\text{C}$  for 50 min. After distillation under reduced pressure at 130  $^\circ\text{C}$  and 0.1 mbar, **SP** was isolated as yellow oil with 96% yield. The global yield of the two step synthesis was therefore about 95%.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}$ -

d6,  $\delta$  in ppm): 2.16 (s, 6H,  $-\text{CH}_3$  at C-2,5 of pyrrole moiety); 3.63 (m, 2H,  $\text{CH}_2\text{OH}$ ); 3.76 (m, 2H,  $\text{CH}_2\text{OH}$ ); 4.10 (quintet, 1H, at C-3 of diol); 4.73 (t, 2H,  $\text{CH}_2\text{OH}$ ); 5.55 (s, 2H, C-3,4 of pyrrole moiety).

#### 4.4. Polymerization reactions

A standard procedure was adopted for polymerization reactions. Entry 3 of Table 1 is reported as an example. **SP** (0.500 g, 2.96 mmol) and **HDI** (0.498 g, 2.96 mmol) were added in sequence in a round bottomed 100 mL flask equipped with a magnetic stirrer, under nitrogen atmosphere. The resulting mixture was then stirred at 90 °C for 150 min. A sample was taken for determining by  $^1\text{H}$  NMR spectroscopy the conversion of the reaction. After cooling at room temperature, the polymer was isolated by dissolution in  $\text{CH}_2\text{Cl}_2$  (2 mL), precipitated from excess diethyl ether (50 mL), filtered, and dried *in vacuo*.

#### 4.5. Preparation of MWCNT-PU adducts

Dispersion of carbon nanotubes in acetone was prepared (1 mg/mL) sonicating for 30 min in a 2 L ultrasonic bath (power 260 W). A PU solution in acetone (1 mg/mL) was added to the previously obtained instable suspension. Upon sonicating for 30 min, a suspension of MWCNT/PU adduct with a concentration of 1 mg/mL was obtained. To verify the stability of such suspension, centrifugation at 5000 rpm was performed for 5 min. The MWCNT-PU adduct powder was obtained by drying the stable suspension at reduced pressure. The mass% of PU in MWCNT-PU adducts was determined to be  $46 \pm 0.5$  for adducts prepared from Entries 2, 3, 4b and 5b.

#### 4.6. Extraction tests with ethyl acetate

100 mg of the MWCNT-PU adduct powder were placed in a round bottomed flask (50 mL) equipped with a magnetic stirring bar and ethyl acetate (25 mL) was added. The ensuing suspension, after being stirred overnight at room temperature, was centrifuged at 5000 rpm for 30 min, and dried under vacuum. The so obtained black powder was analyzed by TGA.

#### 4.7. Investigation of the PU-CNT interaction: $^1\text{H}$ NMR experiments

An NMR tube was charged with 1.5 mL of a previously prepared solution containing **SP** (10 mg) in  $\text{CDCl}_3$ . The tube was inserted into the probe of the NMR spectrometer. After having performed an  $^1\text{H}$  experiment at 298 K, increasing amounts of perylene (1 mg  $\times$  5 times) were added to the solution containing **SP**. NMR spectra were recorded each time after 5 min the addition of perylene.

Perylene (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  in ppm): 7.47 (t); 7.69 (d); 8.20 (d).  
Perylene-**SP** adduct (10 mg **SP**/5 mg perylene) (400 MHz,  $\text{CDCl}_3$ ,

$\delta$  in ppm): 2.27 (s, 6H,  $-\text{CH}_3$  at C-2,5 of pyrrole moiety); 3.97 (m, 4H,  $\text{CH}_2\text{OH}$ ); 4.41 (quintet, 1H, at C-3 of diol); 5.78 (s, 2H, C-3,4 of pyrrole moiety); 7.46 (t); 7.68 (d); 8.19 (d).

#### 4.8. Characterization

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 400 MHz (100 MHz  $^{13}\text{C}$ ) instrument at 298 K. Chemical shifts were reported in ppm with the solvent residual peak as internal standard (DMSO-*d*<sub>6</sub>:  $\delta_{\text{H}} = 2.50$  ppm,  $\text{CDCl}_3$ :  $\delta_{\text{H}} = 7.26$  ppm). Centrifugations were performed using an ALC – Centrifuge 4206.

The number average molecular mass ( $\overline{M}_n$ ), weight-average molecular mass ( $\overline{M}_w$ ) and polydispersity index ( $\overline{M}_w/\overline{M}_n$ ) were determined using a conventional size exclusion chromatography (SEC or GPC) system using tetrahydrofuran (THF) as mobile phase

and a relative calibration constructed with some narrow molecular mass distribution polystyrene (PS) standards. The SEC system consisted of: an Alliance 2695 separation module from Waters, a differential refractometer (DRI) as concentration on-line detector, two PLgel columns from Polymer Laboratories (5  $\mu\text{m}$  of particle size,  $10^4$  and 500 Å of pores size), 0.8 mL/min of flow rate, 100  $\mu\text{l}$  of injection volume, about 3 mg/ml of sample concentration.

DSC analyses under  $\text{N}_2$  (80 mL/min) atmosphere were performed with a Mettler DSC 823e calorimeter. Each sample (4.5 mg  $\pm$  0.05 mg) was kept at 50 °C for 5 min, cooled to  $-85$  °C at 10 °C/min, kept 10 min at this temperature, heated up to 50 °C at 5 °C/min.

TGA tests under flowing  $\text{N}_2$  (60 mL/min) were performed with a Mettler TGA SDTA/851 instrument according to the standard method ISO9924-1. Samples (10 mg) were heated from 30 to 300 °C at 10 °C/min, kept at 300 °C for 10 min, and then heated up to 550 °C at 20 °C/min. After being maintained at 550 °C for 15 min, they were further heated up to 650 °C with an heating rate of 30 °C/min and kept at 650 °C for 20 min under flowing air (60 mL/min).

The FT-ATR spectra were recorded between 450 and 4000  $\text{cm}^{-1}$  by using a Perkin Elmer FT-IR Spectrum One equipped with Universal ATR Sampling Accessory with diamond crystal.

HRTEM analysis of the MWCNT adduct with the PU sample containing the pyrrole ring was performed with a Zeiss Libra<sup>®</sup> 200 FE microscope (Carl Zeiss AG, Oberkochen, Germany) operating at 200 kV and equipped with an in-column OMEGA filter for energy selective imaging and diffraction. Few drops of acetone diluted suspension of the sample were deposited on a holey carbon film supported on a standard Cu grid and air-dried for several hours before analysis.

Wide-angle X-ray diffraction (WAXD) patterns were obtained in reflection, with an automatic Bruker D8 Advance diffractometer, with nickel filtered  $\text{Cu-K}\alpha$  radiation. Patterns were recorded in  $10^\circ$ – $100^\circ$  as the  $2\theta$  range, being  $2\theta$  the peak diffraction angle. Distance between crystallographic planes was calculated from the Bragg law. The  $D_{hkl}$  correlation length, in the direction perpendicular to the hkl crystal graphitic planes, was determined applying the Scherrer equation

$$D_{hkl} = K\lambda/(\beta_{hkl} \cos \theta_{hkl}) \quad (1)$$

where: K is the Scherrer constant,  $\lambda$  is the wavelength of the irradiating beam (1.5419 Å,  $\text{Cu-K}\alpha$ ),  $\beta_{hkl}$  is the width at half height, and  $\theta_{hkl}$  is the diffraction angle. The instrumental broadening,  $b$ , was determined by obtaining a WAXD pattern of a standard silicon powder 325 mesh (99%), under the same experimental conditions. The width at half height,  $\beta_{hkl} = (B_{hkl} - b)$  was corrected, for each observed reflection with  $\beta_{hkl} < 1^\circ$ , by subtracting the instrumental broadening of the closest silicon reflection from the experimental width at half height,  $B_{hkl}$ .

UV-Vis absorption measurements were made using a Hawlett Packard 8452A Diode Array Spectrophotometer.

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