

# Solubilisation of multi walled carbon nanotubes by $\alpha$ -pyrene functionalised PMMA and their liquid crystalline self-organisation†

Stefan Meuer,\* Lydia Braun and Rudolf Zentel

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$\alpha$ -Pyrene functionalised poly(methyl methacrylate) (PMMA) chains were synthesised by RAFT polymerisation and found to be highly efficient to solubilise and disentangle multi walled carbon nanotubes that can now self-organise as liquid crystalline phases in PMMA and PEG 400 matrices.

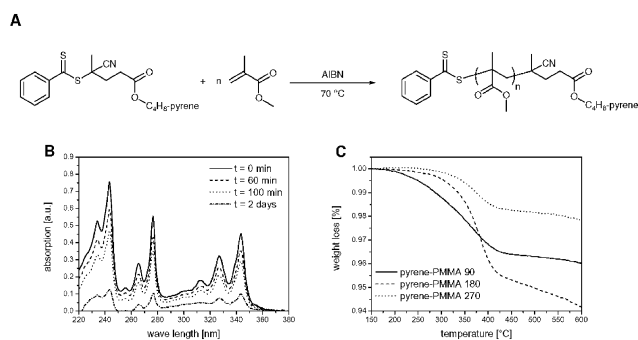
Since the discovery of carbon nanotubes (CNTs) and their unique mechanical and electrical properties, many researchers have investigated ways to solubilise them. The different strategies include chemical modification,<sup>1</sup> covalent attachment of monomers, oligomers and polymers,<sup>2</sup> adsorption of charged surfactants and polyelectrolytes,<sup>3</sup> wrapping with polymers,<sup>4</sup> non-wrapping adsorption of partially collapsed block copolymers<sup>5</sup> and complexation by  $\pi$ - $\pi$  interactions.<sup>6</sup> A major drawback of the chemically functionalised and covalently modified CNTs is the change in their electronic structure by creating sp<sup>3</sup> centres (needed for both methods).<sup>1,2</sup> The same is unfortunately true for CNTs that have adsorbed charged molecules as they usually inject or withdraw electrons from the nanotube.  $\pi$ - $\pi$  Interactions can also change the electronic structure of the nanotubes, especially when heteroatom doped aromatic systems are used. But undoped aromatic systems like pyrene are electronically very similar to graphite as pyrene can be seen as a piece cut from a graphite sheet. In these systems the interaction between two CNTs or different layers of a multi walled carbon nanotube (MWCNT) and between pyrene and CNT is quite similar and does not interfere too much with their electronic structure.<sup>7</sup> Various diblock and statistical copolymers with pyrene anchor units have been investigated by Jérôme *et al.*<sup>8</sup> and Andronov *et al.*<sup>9</sup> who found a strong influence of block architecture, block length and distribution of the anchor units on the adsorption.

From their geometry, CNTs are semi flexible rod-like objects with large persistence length. Thus it should be possible to use them as mesogens in highly concentrated solutions to obtain a liquid crystalline (LC) phase. The experimental observation of the lyotropic phase requires mobility of the nano-objects at high concentration. Thus a neat material of highly anisotropic nano-objects usually does not form LC-phases due to lack of mobility, but LC-phases are formed, if highly concentrated and stable solutions can be obtained. This requires the “solubilisation” of the nano-objects and the choice of a suitable solvent. Thus the concept of “hairy rods”,

which was originally developed for stiff main chain liquid crystals, is also promising for inorganic nano-objects.<sup>10</sup> In this concept, a stiff insoluble core is solubilised by long alkyl chains (the hairs) on its surface. It has recently been used successfully for the functionalisation of TiO<sub>2</sub> nanorods, which act as mesogens at higher concentration.<sup>11</sup>

For the functionalisation of MWCNTs we decided to work with pyrene functionalised polymers.<sup>8,9</sup> As it is known that the molecular weight of the grafts is less important than their grafting density to solubilise nano-objects successfully with polymers we focused on polymer chains that carry exactly one pyrene unit at one end to maximise the number of adsorbed chains. We prepared them using a RAFT (radical addition fragmentation transfer) polymerisation of methyl methacrylate using the pyrene functionalised RAFT agent 4-cyano-4-methyl-4-thiobenzoylsulfanyl-butyric acid 4-pyren-1-yl-butyl ester.<sup>22</sup> Thus each poly(methyl methacrylate) (PMMA) chain is end capped with exactly one pyrene unit (see Fig. 1A). The polymers were analyzed by gel permeation chromatography (GPC) with molecular weights and polydispersity indices reported in Table 1.

The MWCNTs were kindly donated by Bayer Material Science (Baytubes C 150 P, for SEM images of the pristine powder see Fig. 2A and B) and were on average 14.5 nm wide and 1 to 10  $\mu$ m long and were used as received. The adsorption process can be monitored using UV-Vis spectroscopy (see Fig. 1B). For this purpose we prepared a cuvette with pristine MWCNTs lying at the bottom of the cell with a dilute polymer solution above. The absorption of the pyrene units in solution decreases over time as the polymers adsorb onto the MWCNTs at the bottom of the cell. As we worked in very dilute polymer solution, the adsorption is rather slow. In order to investigate the amount of adsorbed polymer chains, the pristine MWCNTs (10 mg) were added to a polymer solution



**Fig. 1** A: Synthesis of pyrene-PMMA; B: UV-Vis absorption kinetics of pyrene-PMMA 90 on MWCNTs; C: TGA analysis of pyrene-PMMA functionalised MWCNTs.

Institute for Organic Chemistry, University of Mainz, Duesbergweg 10-14, 55128 Mainz. E-mail: zentel@uni-mainz.de; Fax: +49 6131 3924778; Tel: +49 6131 39225873

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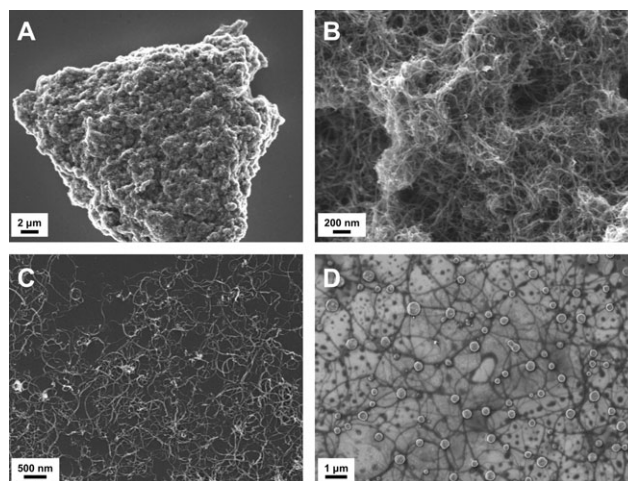
**Table 1** Molecular weight and adsorption characteristics of  $\alpha$ -functionalised PMMA

Name	Repeat units	$M_n/g\ mol^{-1}$	PDI	Adsorbed polymer on MWCNTs/wt%	Chains per MWCNT	$s/nm$
<b>pyrene-PMMA 90</b>	90	8900	1.18	3.8	3000	9
<b>pyrene-PMMA 180</b>	180	18 100	1.31	4.1	1550	12
<b>pyrene-PMMA 270</b>	270	27 200	1.35	1.8	500	22

in THF (2 mg in 2 ml) and stirred over night. The MWCNTs were separated by centrifugation and redispersed in fresh THF to remove unbound polymer chains. The procedure was repeated three times. The MWCNTs were then dried and investigated by thermo gravimetry (TGA, under nitrogen atmosphere, see Fig. 1C). The PMMA chains decompose between 300–400 °C and the weight loss is measured. Out of this mass, the number of chains that adsorbed per MWCNT can be calculated (see Table 1). For the calculations we assumed an average surface per MWCNT of around  $2.3 \times 10^5\ nm^2$  (assuming an average length of 5  $\mu m$  and width of 14.5 nm). The number of MWCNTs is estimated to be  $8.6 \times 10^{11}\ mg^{-1}$  (assuming a density of  $1400\ kg\ m^{-3}$  and a volume of  $8.3 \times 10^5\ nm^3$  per MWCNT). The interpolymer distance  $s$  between adsorbed polymers can be calculated as the square root of the surface area per polymer chain.<sup>12</sup>

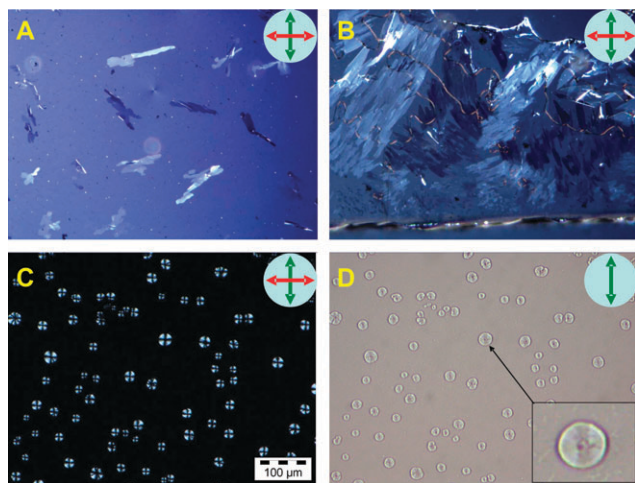
On first view, the **pyrene-PMMA 180** was adsorbed best as by TGA analysis 4.1 wt% polymer was adsorbed. For **pyrene-PMMA 90** 3.8 wt% and for **pyrene-PMMA 270** 1.8 wt% polymer were found after functionalisation of the MWCNTs. But the total number of adsorbed chains is due to the different molecular weights, largest for **pyrene-PMMA 90** with around 3000 chains. For **pyrene-PMMA 180** around 1550 and for **pyrene-PMMA 270** around 500 adsorbed chains per MWCNT were found (see Table 1). The interpolymer distance  $s$  was calculated to be 9 nm for **pyrene-PMMA 90** and increased to 22 nm for **pyrene-PMMA 270**. Thus the shortest polymer adsorbs significantly better than the longer polymer chains. This effect might be due to a stronger tendency of longer polymer chains to desorb from the surface as the hydration enthalpy increases with growing chain length and overcomes the binding energy of the single anchor unit. This phenomenon was also found in grafting from polymers started by a pyrene anchored ROMP catalyst. With increasing polymer chain length the polymer films became unstable and vanished into solution.<sup>13</sup> This cannot be detected in our systems but a weakening of the interaction can be stated from the TGA data. Nevertheless all polymers were capable of stabilising MWCNT dispersions in THF. The amount of polymer needed for a stable dispersion is just around 10 wt% of the carbon nanotubes (ratio  $M_{MWCNT} : M_{pyrene-PMMA} = 10 : 1$ ) which is much less than reported in the literature.<sup>5,8,9</sup>

Starting with the pristine and highly entangled MWCNTs (see Fig. 2A and B) is challenging as disentanglement is crucial for all applications. Fig. 2C shows a dried solution of **pyrene-PMMA 90** stabilised MWCNTs. The MWCNTs have been disentangled in the polymer solution and were forming a spreaded film of individual nanotubes upon solvent evaporation. The **pyrene-PMMA 90** polymer chains were able to functionalise and mobilise the nanotubes sufficiently that they disentangled upon ultra sonification. Moreover they were then

**Fig. 2** SEM Images of A, B: pristine MWCNTs; C: **pyrene-PMMA 90** functionalised MWCNTs drop coated from solution; D: **pyrene-PMMA 90** functionalised MWCNTs in an etched PMMA film.

stabilised in solution and formed dispersions in THF that were completely stable (no sedimentation observable over weeks). When more polymer is added than needed for the surface functionalisation (ratio  $M_{MWCNT} : M_{pyrene-PMMA} = 1 : 30$ ), polymer films can be fabricated by spin coating from solution with well dispersed MWCNTs as filler material. In order to visualise the carbon nanotubes, the PMMA excess was etched away by oxygen plasma and the MWCNTs remained on the substrate (see Fig. 2D). Residual polymer droplets can be seen and a percolation network of carbon nanotubes appears after etching. This is an absolute necessity to enhance the mechanical and electrical properties of the matrix with carbon nanotubes as filler.<sup>14–18</sup> Thus we were able to mediate successfully between the MWCNTs and the PMMA film and obtained a homogeneous film with embedded percolated nanotubes.

As the MWCNTs resemble semi flexible rod-like objects it should be possible to use them as mesogens to obtain a liquid crystalline phase in analogy to what is known from solutions of rigid-rod polymers. Really highly concentrated solutions of polymer functionalised MWCNTs in PMMA (excess **pyrene-PMMA 90** polymer,  $M_{MWCNT} : M_{pyrene-PMMA} = 1 : 1$  or  $3 : 1$ ) prepared *via* solvent casting gives inhomogeneous films, which show highly birefringent areas (Fig. 3A and B) in an isotropic matrix. These areas are oriented as the birefringence is angle dependant and they become completely dark for a certain angle. These patches cannot result from the end group functionalised atactic polymer as it does not crystallise and therefore it can only be built up by oriented and densely packed MWCNTs. In the films with lower ratio of MWCNTs to functionalised polymer ( $M_{MWCNT} : M_{pyrene-PMMA} = 1 : 1$ , see



**Fig. 3** Polarised microscopy images of A, B: pyrene-PMMA 90 functionalised MWCNTs in PMMA films (crossed polarisers); C: LC droplets of pyrene-PMMA 90 functionalised MWCNTs in PEG (crossed polarisers); D: same area as in C but without analyzer.

Fig. 3A), the patches have a quite irregular shape and the birefringence vanishes for certain angles. In the films with the higher ratio of MWCNTs to functionalised polymer ( $M_{\text{MWCNT}} : M_{\text{pyrene-PMMA}} = 3 : 1$ ), the patches start to interact with each other. We observed areas where many close lying patches are oriented in the same direction (their birefringence vanishes for the same angle, see Fig. 3B).

As the nanotubes are frozen in these PMMA films after solvent evaporation, their dynamic behaviour could not be investigated. This can be changed by using oligomeric matrices that are still mobile but on the other hand do not evaporate like a solvent. In another work, we found PEG 400 ( $M_n = 400 \text{ g mol}^{-1}$ ) to be a suitable matrix for PMMA functionalised  $\text{TiO}_2$  nanorods.<sup>11</sup> Also pyrene-PMMA 90 is miscible with PEG 400 (see ESI†). We prepared a mixture with a ratio of  $M_{\text{pyrene-PMMA 90@MWCNT}} : M_{\text{PEG400}} = 1 : 1$  in THF and evaporated the solution on a glass slide. We found a birefringent phase by polarised microscopy which was viscous but still mobile and showed a loss of the birefringence upon heating over 48 °C. The birefringence recovered after cooling and tempering around 20 °C produced liquid crystalline droplets (see Fig. 3C). The formation of droplets was—in this case—simply due to a lack of material in order to form a complete film. These droplets show textures that are common for nematic phases with a radial orientation of the mesogens (MWCNT).<sup>19</sup> When the analyzer is removed, the droplets show a darker area parallel to the incident polarisation plane (see Fig. 3D). This is due to the ability of carbon nanotubes to absorb light along their long axis.<sup>20</sup> Assemblies of carbon nanotubes are known as potential materials for the polarisation of light which could be found in these droplets as well as in literature known organic liquid crystals that were filled with carbon nanotubes.<sup>21</sup> Thus we were able to solubilise and mobilise the MWCNTs sufficiently to create a liquid crystalline phase out of the nanotubes themselves.

To conclude, we presented a synthetic route to  $\alpha$ -functionalised polymers via a pyrene functionalised RAFT agent. We

showed that thus functionalised MWCNTs become disentangled and separated nanotubes are found.

At high concentration the functionalised MWCNTs self organise into oriented domains in PMMA as well as in PEG 400 matrices. In the PEG 400 matrix we found a liquid crystalline phase of the nanotubes, that act as mesogens. This offers the potential to align carbon nanotubes at high volume fractions.

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