



α -Pyrene polymer functionalized multiwalled carbon nanotubes: Solubility, stability and depletion phenomena

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ABSTRACT

This paper presents a study on the stability of dispersions of multiwalled carbon nanotubes that are covered with α -pyrene functionalized polymers prepared via reversible addition–fragmentation chain transfer (RAFT) polymerization and dispersed in different solvents. We find that a rather small amount of these polymers ($M_{\text{polymer}}/M_{\text{CNT}}$ less than 0.1) is capable of stabilizing a high concentration of CNTs (up to 2500 mg/l) in solution. Another strong evidence for well-stabilized CNTs is the comparably low gel points of around 1 vol% of CNTs in solution. We find that adding the α -pyrene functionalized polymer to CNTs has two counter playing effects: on the one hand, increased surface coverage of the carbon nanotubes increases their solubility; on the other hand increased concentration of free polymer in the solution enhances the depletion forces between the nanotubes.

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1. Introduction

Carbon nanotubes (CNTs) have mechanical, electrical, thermal and optical properties that make them highly interesting for applications in materials science [1,2]. “Raw” nanotubes, however, are usually produced in the form of a disordered powder, in which the individual CNTs are highly entangled. This applies for single walled carbon nanotubes and for their – not as well defined, but easier accessible – multiwalled form. In order to use them in technical applications, it is thus necessary to disperse them in a solvent. Once they are dispersed, they can be mixed with other substances to form composites, squeezed into fibres or deposited as a film on a substrate. Dispersing nanotubes is, however, not easy, as they strongly attract each other via van der Waals forces. A variety of methods for chemical functionalization as well as physical methods have been used to disperse carbon nanotubes. The different strategies include chemical modification [3], covalent attachment of monomers, oligomers and polymers [4], adsorption of charged surfactants and polyelectrolytes [5], wrapping with polymers [6], non-wrapping adsorption of partially collapsed block copolymers [7] and complexation by π – π interactions [8]. A major drawback of the chemically functionalised and covalently modified CNTs is the

change in their electronic structure by creating sp^3 centres (needed for both methods) [3,4]. The same is unfortunately true for CNT that adsorbed charged molecules as they usually inject or withdraw electrons from the nanotube. Large aromatic systems like pyrene are electronically very similar to graphite as pyrene can be seen as a cut piece from a graphite sheet. In these systems the interaction between two CNTs or different layers of a multiwalled carbon nanotube (MWCNT) and between pyrene and CNT is quite similar and does not interfere much with their electronic structure [9].

Surfactants have been used extensively to stabilize CNTs in water leading to very high solubilities of CNTs in water up to 20 mg/ml [10–12]. They usually use more surfactant than CNTs having functionalization ratios of surfactant to CNT of 10:1, which is a consequence of strong adsorption/desorption equilibria. A serious drawback of electrostatically stabilized CNTs (either by oxidation or surfactant treatment) is that their solubility is limited to aqueous media and that the charges used for stabilization disable any use for electronic devices (short cuts created by the counter ions). Therefore ion free dispersions in organic solvents are highly desired but require another stabilization approach.

For this purpose the particles have to be surface functionalized with an organically soluble corona to overcome the strong adhesion forces. This can be done using the concept of “hairy rods”, which was originally developed for stiff main chain liquid crystalline polymers and which is very promising for such inorganic nano-objects too [13]. In that concept, a stiff insoluble core is solubilised by linking long chains (the hairs) on its surface. In our case, polymer chains are these hairs leading to a steric stabilization as well as organic solubility. As polymers themselves are objects of nanometre dimensions,

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polymer coated surfaces are stabilized sterically up to distance of nanometres and not just for angstroms as with alkyl chains. In addition, new polymers designed for surface functionalisation have multiple anchor units for surface attachment. Therefore adsorption–desorption equilibria reactions are avoided and a robust fixation of the multi-dentate polymer ligand to the surface can be achieved. In addition polymers can be prepared with complex functions as stimuli responsive behaviour or conductive properties. On the other hand, polymer functionalized CNTs can be incorporated and distributed homogeneously into polymer matrices. For surfactant stabilized systems this is hard to realize as the surfactant has to be fully miscible with the polymer matrix.

Various polymers with pyrene anchor units have been investigated by Jérôme et al. [14] and Andronov et al. [15] and were used to disperse carbon nanotubes. Our approach is different from these ones as we use a pyrene functionalized RAFT agent to synthesize α -pyrene functionalized polymers. Thus we can use the same method to polymerize different monomers with exactly the same anchoring system. This method was used recently to disperse multiwalled carbon nanotubes very efficiently and liquid crystalline ordering was found [16].

In this article we present a study on the stability of dispersions of multiwalled carbon nanotubes (Baytubes[®]) that are functionalized with α -pyrene functionalized polymers in different solvents and in the presence of additional “free” polymer. We interpret our results within the framework of a “semi-flexible rod plus depletant” model. We find that adding the α -pyrene functionalized polymer to the suspensions has two counter playing effects on the nanotubes: on the one hand, increased surface coverage of the carbon nanotubes increases their solubility; on the other hand increased polymer concentration in the solution enhances the depletion attraction between the nanotubes.

2. Results and discussion

2.1. Polymer synthesis

The synthesis of the α -pyrene functionalized polymers is based on the reversible addition–fragmentation chain transfer (RAFT) polymerization, a controlled radical polymerization allowing the synthesis of polymers with polydispersities around 1.2 and building up block copolymers [17]. We use a pyrene-functionalized RAFT agent to mediate the polymerization of methyl methacrylate (MMA) and diethylene glycol monomethyl ether methacrylate (DEGMEMA). It is made by DCC (*N,N'*-dicyclohexyl carbodiimide) coupling of (4-cyanopentanoic acid)-4-dithiobenzoate (synthesized according to literature [18]) with 4-pyren-1-yl-butan-1-ol. As

the monomers are inserted into the carbon sulphur bond of the RAFT agent, the pyrene moiety stays at exactly one end of the polymer chain and α -pyrene functionalized polymers pyrene–PMMA and pyrene–PDEGMEMA are formed (see Fig. 1).

The resulting end group functionalized polymers were analyzed by gel permeation chromatography (GPC) and polydispersity indices (PDI) around 1.2 were found, indicating a controlled polymerization mechanism with this functionalized RAFT agent (see Fig. 2). Molecular weights and polydispersities are given in Table 1. The GPC elugram of pyrene–PDEGMEMA is showing a small shoulder on the left side indicating some side reactions occurring, but the polydispersity is still fairly low with 1.25. Remarkable is the fact that both detectors detect the polymers. Normally, PMMA and PDEGMEMA can only be detected by the refractive index detector, as no UV absorbing moiety is present at 255 nm. With the pyrene unit being covalently bound to the end of the polymer, the UV detection is now very easy and the signals can be recorded by both detectors equally. The tiny shift in elution volume is due to the fact that the sample passes the UV detector prior to the refractive index detector.

2.2. PMMA functionalized carbon nanotubes in THF

The carbon nanotubes (CNTs) used in this work are multiwalled (3–15 walls) and in average 14.5 nm wide and 1–10 μm long. They were kindly donated by Bayer Material Science AG (Baytubes C 150 P) and were used as-received. We focused on these less perfect CNTs as they can be produced in ton scale for a reasonable price making them very prominent for mass scale real world applications. In order to investigate the amount of adsorbed polymer chains, the pristine entangled CNTs (10 mg) were added to a polymer solution in THF (10 mg in 2 ml) and stirred over night. No ultrasound was applied for easy collection of the CNTs. Of course, this treatment is not useful for the preparation of a dispersion, but for an adsorption analysis. The CNTs were separated by centrifugation and washed with fresh THF to remove unbound polymer chains. The procedure was repeated three times. The CNTs were then dried and investigated by thermogravimetry (TGA, under nitrogen atmosphere, see Fig. 6). The PMMA chains decompose between 300 and 400 °C and the weight loss is measured. Thus the amount of pyrene–PMMA that bounds per mg of CNTs is found to be 0.03 mg. We investigated this value for different concentrations of the functionalization polymer and found no concentration dependency when using more than 2 mg of pyrene–PMMA per 10 mg nanotubes. This value corresponds to a coverage of approximately 1200 polymer chains per nanotube and an inter-polymer distance of 14 nm (the calculations are based on a 5 μm long and 14.5 nm wide nanotube with a surface of $2.3 \times 10^5 \text{ nm}^2$ and

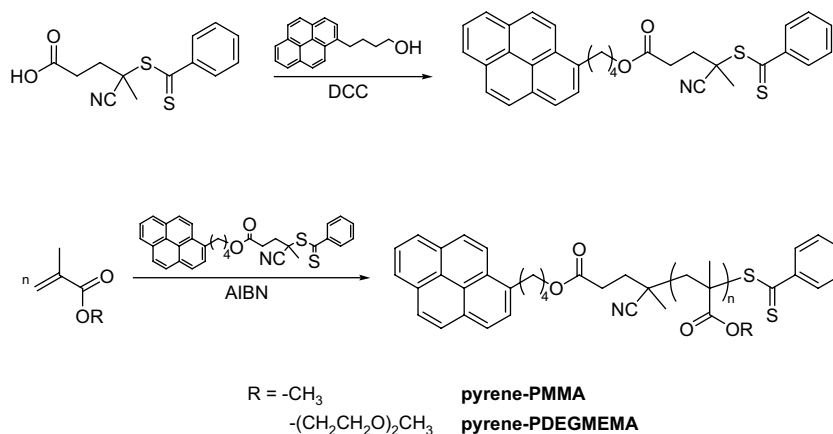


Fig. 1. Synthesis of α -pyrene functionalized polymers.

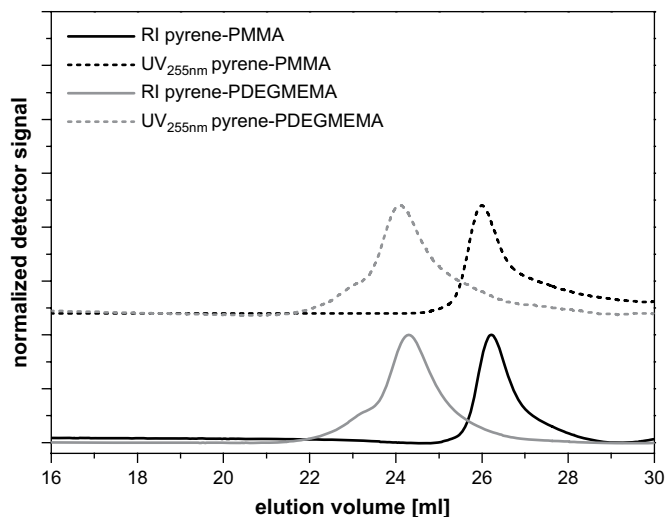


Fig. 2. GPC elugram of both α -functionalized polymers. The detectors shown are a refractive index (RI) detector and an UV detector ($\lambda = 255$ nm).

a volume of $8.3 \times 10^5 \text{ nm}^3$. The density of the nanotubes is 1400 kg/m^3 so that there are around 8.7×10^{11} nanotubes present per mg). Therefore, an adsorption of 0.03 mg polymer per mg CNTs correlates to a coverage of 0.015 mg/m^2 .

To investigate the stability of pyrene-PMMA functionalized CNTs in solution we prepared samples with various concentrations of CNTs and pyrene-PMMA and sonified them for 5 min at 20 W (to disentangle the CNTs). The results are presented in Fig. 3A. Starting from unstable dispersions at polymer concentrations too low to coat the CNTs, we found stable dispersions at higher polymer concentrations, where the CNTs could not be centrifuged down, but also unstable dispersions at still higher polymer concentrations, that precipitated quickly over an hour. These unstable dispersions do not pass a $5 \mu\text{m}$ meshed syringe filter indicating that the aggregates are larger than $5 \mu\text{m}$. A stable dispersion passes the filter.

On the other hand we also found totally gelled samples on high CNT concentrations. With the known adsorption of pyrene-PMMA on the CNTs we were able to calculate the excess polymer concentration in solution (see Fig. 3B).

At first: we found stable dispersions up to concentrations of PMMA functionalized CNTs larger than 2.5 mg/ml . Solubilities known from literature for polymer stabilized CNTs in organic solvents are as high as 0.65 mg/l and as low as 0.05 mg/l [19,20]. The solubility of these polymer stabilized dispersions was so far achieved with ratios of polymer to CNTs around 1–2 [14,15]. We were able to achieve a solubility of 2.5 mg/l with a functionalization ratio less than 0.1 (0.075 mg pyrene-PMMA were sufficient to stabilize 2.5 mg CNTs). The solubility achieved with our system is higher than for other polymers, but lower than literature reported high score solubilities for surfactant stabilized CNTs in water, for which [12] up to 10 and 20 mg/ml [10] can be achieved with functionalization ratios of 1:1 [12] and 10:1 [10] (surfactant:CNT). However as already mentioned in the introduction, ion stabilized systems in water are not suitable for electronic applications or the incorporation of CNTs into polymers.

Table 1
Polymer characterization.

Polymer	M_n^a [g/mol]	M_w^a [g/mol]	PDI ^a
Pyrene-PMMA	16,200	18,800	1.16
Pyrene-PDEGMEMA	63,000	78,800	1.25

^a Determined by GPC in THF.

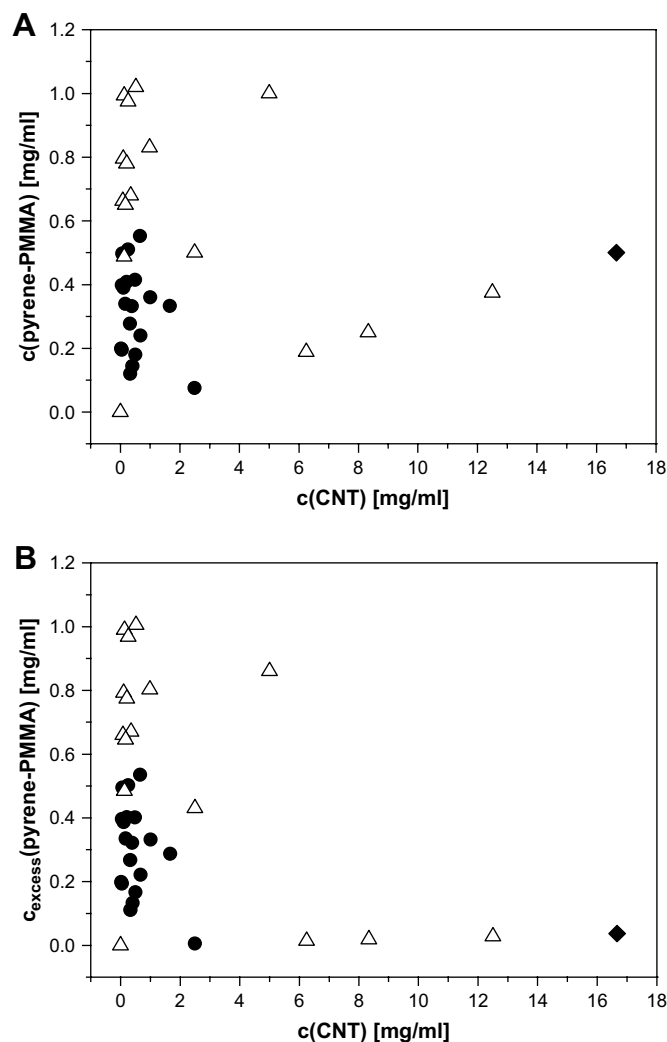


Fig. 3. ● stable, Δ unstable and \blacklozenge gelled dispersion. Phase diagram of CNT versus (A) pyrene-PMMA concentration; (B) pyrene-PMMA excess concentration in THF solution.

Secondly, we reached a gel region upon 16.6 mg/ml . This indicates that the CNTs are starting to fill the whole volume of the solution by a percolated network at volume fractions of around 1.2% (corresponding to 16.6 mg/ml as the density of the CNTs is approximately 1.4 g/ml). This value is comparable to natural gellators as gelatine (forms stable gels at approx. 1 vol% in water) [21].

Interestingly the dispersion becomes unstable upon an excess polymer concentration of 0.6 mg/ml . This effect is known from theoretical considerations for mixtures of rods and spheres. In a very simple, purely entropic model that is based on the Asakura-Oosawa model, [22] the spheres entropically mediate an effective attraction between the rods. This effect is known as depletion and plays a very important role in all polymer stabilized colloidal systems. The quintessence of this phenomenon is that adding more stabilizing polymer than needed is counterproductive and results in poor or even unstable dispersions [23]. In the field of CNT dispersions a very interesting review on depletion was published by Poulin and Zakri [24]. Another evidence for depletion is the reversibility as the data points shown have been prepared by dilution of dispersions, which have been unstable first and became stable upon dilution.

In the diagrams shown in Fig. 3, the excess polymer was unbound functionalization polymer. To generalize our observations we added polyethylene glycol (PEG) of different molecular weight to a stable dispersion from Fig. 3 (0.18 mg/ml pyrene-PMMA and

0.5 mg/ml CNTs). The images of these dispersions are shown in Fig. 4 and in each set of 2 ml vials 0.2, 1 and 10 mg of PEG 2000, 5000 or 20,000 were added. As PEG and PMMA are well known to have a Flory–Huggins interaction parameter of almost zero, one can be sure that the effects observed are of entropic nature only [25].

Upon addition of PEG 2000 no change in stability can be observed, even upon addition of 10 mg. PEG 5000 shows some concentration dependence as 0.2 mg do not disturb the stability, whereas upon 1 and 10 mg PEG 5000 addition depletion starts. This can be explained by the fact that the PEG 5000 used is polydisperse so that the size of some chains is comparable to the size of the functionalization polymer on the CNT surface. For PEG 2000 no chain is big enough to be hindered in its diffusion between PMMA grafted CNTs. For PEG 20,000 almost all chains are larger than the polymer corona around the CNTs and depletion sets in already for the smallest additions (0.2 mg).

2.3. PDEGMEMA functionalized carbon nanotubes in water

The adsorption of pyrene–PDEGMEMA was investigated with the same method as for pyrene–PMMA and an adsorption of 0.40 mg per mg of CNTs was found from THF solutions (see Fig. 6). This corresponds to a coverage of 4400 chains per nanotube, an inter-polymer distance of 7 nm and an adsorption of 0.20 mg/m² (based on the same calculations as for pyrene–PMMA). This polymer adsorbs better on the CNTs and it can be assumed that unspecific binding of PDEGMEMA plays a role too. PDEGMEMA offers the possibility to disperse CNTs not only in THF, but also in polar solvent like alcohols

and it has a lower critical solution (LCST) behaviour in water. The LCST temperature is around 25 °C and allows switching of the polymer corona from a theta-like dissolved to a collapsed precipitated state. Therefore we especially investigated the stability of pyrene–PDEGMEMA functionalized CNTs in aqueous solutions below 25 °C. We prepared various concentrations of CNTs and pyrene–PDEGMEMA and formed dispersions by sonification at 20 W for 5 min. We were able to find again stable, unstable and gelled dispersions as discussed before for pyrene–PMMA functionalized CNTs in THF. The solubility of the CNTs was 2.65 mg/ml at a polymer concentration of 3.76 mg/ml, which is again significantly higher than literature known solubilities. The functionalization ratio is around 1.4, which is significantly larger than for pyrene–PMMA, but still in the typical range of literature known dispersions with much smaller CNT solubilities. At high concentrations of CNT gelled samples are found (see Fig. 5D). SEM images of the dried gel show large entangled structures indicating an unordered percolation of single nanotubes. The gel point is higher than for pyrene–PMMA but still fairly low around 25 mg/ml or 1.7 vol%, which is reasonable as water is not an as good solvent for PDEGMEMA as THF for PMMA.

The whole phase diagram is shown in Fig. 5A. It shows a re-entrant behaviour, which is much more pronounced as discussed for the PMMA functionalized CNTs. With increasing amount of pyrene–PDEGMEMA the dispersions are first unstable (up to 0.1 mg/ml), then stable (up to 8.3 mg/ml) and then unstable again (over 10 mg/ml). To investigate this effect, we determined the adsorbed amount of pyrene–PDEGMEMA on nanotubes exposed to different concentrations of the polymer in water (constant concentration of

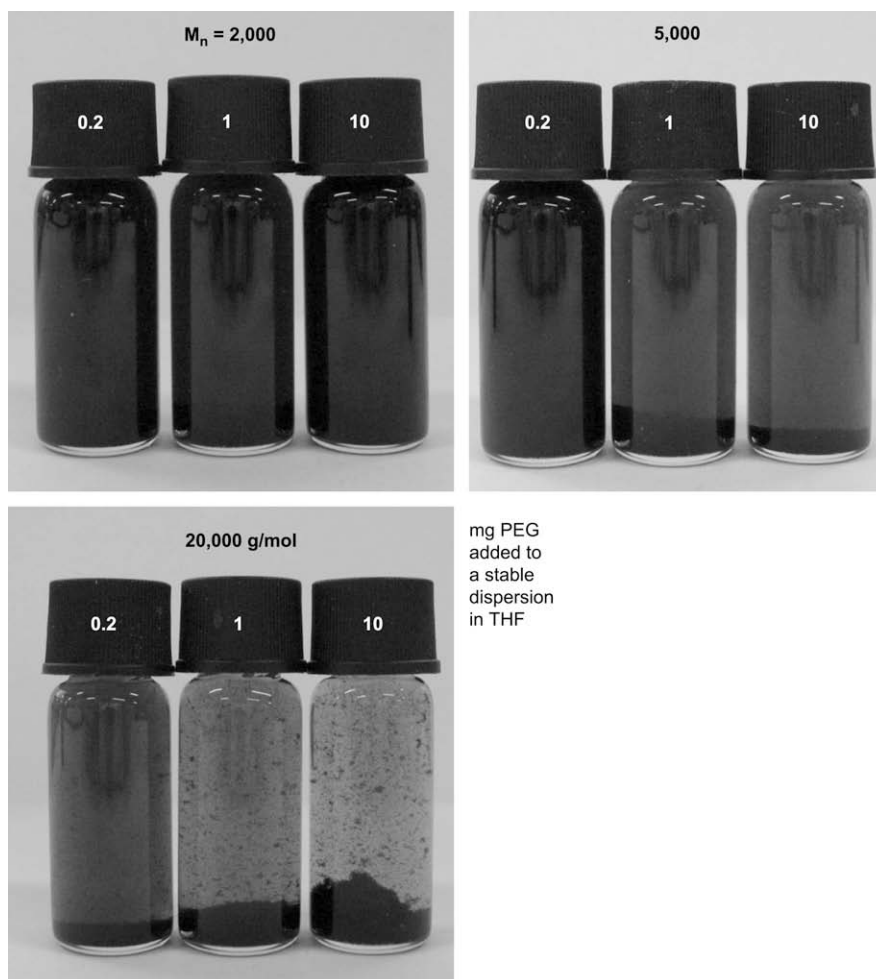


Fig. 4. Depletion of pyrene–PMMA functionalized carbon nanotubes by PEG.

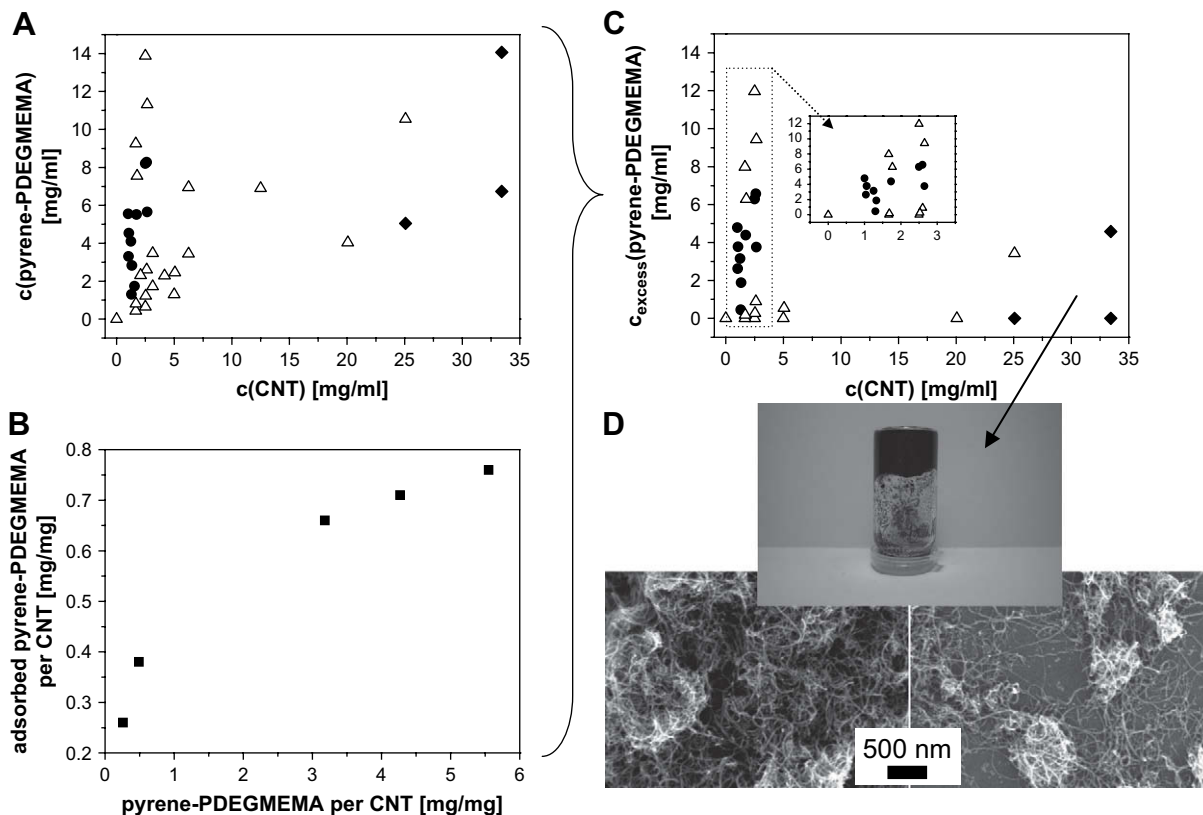


Fig. 5. ● stable, △ unstable and ◆ gelled dispersion. (A) Phase diagram CNT concentration versus pyrene–PDEGMEMA concentration; (B) Adsorption behaviour of pyrene–PDEGMEMA in water (used to calculate Fig. 5C); (C): Phase diagram CNT concentration versus pyrene–PDEGMEMA excess concentration in water; (D) Images of a sample in the gel region (lower images of a dried gel taken by a SEM).

nanotubes $c(\text{CNT}) = 3 \text{ mg/ml}$). The CNTs were collected by centrifugation and washed from unbound polymer two times with water. In this case there is a clear dependency of the amount of bound polymer (see Fig. 5B) on the preset ratio of polymer to CNT. This is different from the experiments in THF. We assume that this additional unspecific adsorption happens due to the following reasons: first, PDEGMEMA is soluble in water, but close to an LCST. This means that the polymer is not in a good solvent. Second, carbon nanotubes are hydrophobic leading to a high surface tension with polar solvents like water. This leads to additional unspecific adsorption of polymer and an adsorption/desorption equilibrium which is concentration dependent. This effect will not be present in good solvents for the functionalization polymer (like THF) and when the surface tension between CNT and solvent is moderate. With the adsorption information from Fig. 5B we rescaled the phase diagram to show the excess concentration of pyrene–PDEGMEMA in Fig. 5C (the inset enlarges the re-entrant zone). In this rescaled diagram the re-entrant behaviour is restored. It seems that a small amount of “free” or excess polymer is needed in solution to solubilise the nanotubes. We believe that this is due to the adsorption–desorption

equilibrium. In order to coat the CNTs sufficiently some free polymer is needed in solution, but too much free polymer leads to segregation because of the depletion effect. Additionally, depleted CNTs might form a lyotropic liquid crystalline phase, which have been found for a similar system in a former work [16] and could be another explanation for the dispersion instability.

Directly correlated to the results from Fig. 5B (concentration dependent adsorption) are the results shown in Table 2. Here we calculated the number of chains per CNT based on the TGA experiments shown in Fig. 6. The number of adsorbed chains increases

Table 2
Surface coverage of pyrene–PDEGMEMA on carbon nanotubes.

Pyrene–PDEGMEMA per CNT ^a [mg/mg]	Chains per CNT ^b	Adsorption ^b [mg/m ²]	A_{chain}^b [nm ²]	s^b [nm]	σ^{*b}
0.26	2900	0.13	79	8.9	2.6
0.49	4200	0.25	55	7.4	3.8
3.18	7300	1.60	31	5.6	6.6
4.27	7900	2.17	29	5.4	7.2
5.55	8500	2.82	27	5.2	7.7

^a Measured by TGA, see Fig. 6.

^b Assuming an average length of 5 μm and width of 14.5 nm.

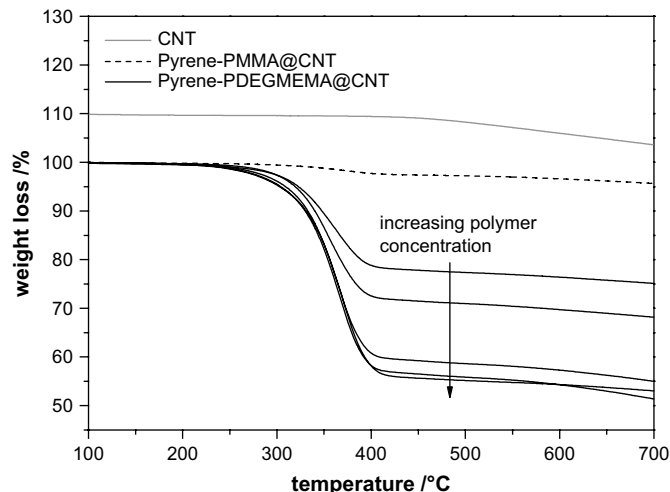


Fig. 6. TGA traces of pure CNTs, pyrene–PMMA and pyrene–PDEGMEMA functionalized CNTs, measured under nitrogen and a heating rate of 20 °C/min.

from 2900 to 8500 chains and the inter-polymer distance is decreased from 8.9 to 5.2 nm in this concentration series. This is close to the radius of gyration of the functionalization polymer pyrene-PDEGMEMA (8.1 nm) so that the reduced coverage $\sigma^* (= \pi R_g^2 / A_{\text{chain}})$ increases from 2.6 to 7.7.

The TGA traces (see Fig. 6), which were used for the calculations presented before, show a distinct separation of CNT decay (above 480 °C) and polymer decay (below 400 °C). Therefore, the amount of bound polymer can be analyzed by measuring the weight loss before 400 °C and is not affected by the CNT decay.

3. Conclusions

Dispersions of polymer-functionalized carbon nanotubes show a rich phase behaviour. Mainly, there are two counter playing effects of the amount of polymer added for functionalization: With increasing amount of polymer the nanotubes become better coated (the grafting density increases). Hence their solubility increases and their gel point decreases. On the other hand, excess polymer in the solution causes depletion attraction between the nanotubes and hence increases their tendency to aggregate. In detail, we showed that a very little amount of pyrene-PMMA ($M_{\text{polymer}}/M_{\text{CNT}}$ less than 0.1 compared to literature known ratios of 1 to 2) [14,15] is capable to stabilize very large concentrations of CNTs (up to 2.5 mg/ml compared to literature known 0.5–0.65 mg/ml) [19,20] in solution. We found that functionalization ratios of 1 or 2 already lead to a strong depletion force and unstable dispersions are formed. Another strong evidence for well-stabilized CNTs are the comparably small gel points of around 1 vol% in solution. As this can only be achieved by fully disentangled nanotubes, the stabilization must have been very good.

The differences between pyrene-PMMA and pyrene-PDEGMEMA can be rationalized by the following scenario: Pyrene-PMMA in THF is selectively linked at one end of the chain via the pyrene unit to the CNT and extends therefore highly into the solution. Therefore we observed stable dispersions with small amounts of pyrene-PMMA. For PDEGMEMA, however, binding to the CNTs might be different as we found (a) that a significantly larger amount of pyrene-PDEGMEMA binds to the surface and (b) that the adsorption is concentration dependent. Thus we believe, that pyrene-PDEGMEMA does not only adsorb selectively via the terminal pyrene unit, but also unspecifically via the diethylene glycol side group moieties of the chains. Under these conditions the conformation of a pyrene-PDEGMEMA chain on the surface of a CNT will be different from pyrene-PMMA. It might wrap around the CNTs and extend only little into the solution. Thus more adsorbed polymer would be needed to stabilize the nanotubes as we found experimentally. Water as solvent for PDEGMEMA is also a special case: As the CNTs are rather hydrophobic the unspecific adsorption is enhanced and a concentration dependence is found. This is due to an adsorption-desorption equilibrium and a stable polymer adsorption requires the presence of free excess polymer in solution. This is of course also leading to depletion, as we found for larger polymer concentrations.

We hope that these effects can be used to tailor the properties of carbon nanotube suspensions towards specific technological applications.

4. Experimental

The CNTs were kindly donated by Bayer MaterialScience AG (Baytubes C 150 P) and used as received. They are to our best knowledge and according to Bayer MaterialScience AG free of amorphous carbon and fullerenes and they have a carbon purity of more than 95% (elemental analysis). Another evidence for the

absence of amorphous carbon is the TGA trace showing no weight loss up to 500 °C. Also, free amorphous carbon could not be found by own SEM images and provided TEM images. All solvents were dried and distilled before use. Methyl methacrylate (from Acros) and (diethylene glycol monomethyl ether)-methacrylate ((2-methoxy-ethoxy)-ethyl methacrylate from Aldrich) were distilled before usage, α, α' -azoisobutyronitrile (AIBN, from Fluka) was recrystallized from diethyl ether, dioxane and tetrahydrofuran (THF) were dried and distilled before usage, all other solvents were used without further purification. Gel permeation chromatography (GPC) was carried out in THF as solvent and the detector system contained refractive index (Jasco RI 1570), UV-vis (Jasco UV 1575) and light scattering (Wyatt miniDAWN) detectors. Thermogravimetry (TGA) was carried out in a Perkin Elmer Pyris 6 TGA under nitrogen atmosphere and analyzed by the Pyris software. Sonication was done using a Branson Digital Sonifier (model 250-D) tip-generator with a power of 10 W for 15 min.

Synthesis of 4-cyano-4-methyl-4-thiobenzoylsulfanyl-butylric acid 4-pyren-1-yl-butyl ester (pyrene functionalized RAFT agent, modified from Ref. [18]): 204 mg (0.73 mol) (4-cyanopentanoic acid)-4-dithiobenzoate (synthesized according to Ref. [18]), 200 mg (0.73 mol) 4-(1-pyrenyl)-butanol and 9 mg (0.073 mol) 4-(dimethylamino)-pyridine were dissolved in 5 ml THF and a solution of 151 mg (0.73 mol) DCC (*N,N'*-dicyclohexyl carbodiimide) in 3 ml CH_2Cl_2 was added at 0 °C. The mixture was stirred and allowed to warm up to room temperature overnight. The suspension with white precipitate was filtered over Celite, washed with chloroform and purified by column chromatography (pure chloroform). The product, 4-cyano-4-methyl-4-thiobenzoylsulfanyl-butylric acid 4-pyren-1-yl-butyl ester, was freeze dried from benzene (366 mg, 95%). δ_{H} (100 MHz; CDCl_3 ; Me_4Si) 8.23 (1H, d, pyrene-H), 8.13 (4H, q, pyrene-H), 8.01 (3H, s, pyrene-H), 7.84 (3H, m, phenyl-H + pyrene-H), 7.53 (1H, t, phenyl-H), 7.35 (2H, t, phenyl-H), 4.16 (2H, t, C_4H_8), 3.37 (2H, t, C_4H_8), 2.72–2.58 (2H, m, C_4H_8), 2.01–1.66 (9H, m, $\text{C}_4\text{H}_8 + \text{CH}_3 + \text{C}_2\text{H}_4$).

Synthesis of α -pyrene functionalized polymers pyrene-PMMA and pyrene-PDEGMEMA. General procedure: monomer, RAFT agent (4-cyano-4-methyl-4-thiobenzoylsulfanyl-butylric acid 4-pyren-1-yl-butyl ester) and AIBN (α, α' -azoisobutyronitrile) were dissolved in 2 ml dioxane. Oxygen was exchanged by nitrogen by five freeze-pump-thaw cycles. Polymerization was carried out at 70 °C for 20 h. The polymers were purified by dissolving in THF and precipitating in methanol for pyrene-PMMA and hexane for pyrene-PDEGMEMA for three times. Molecular weights and PDIs are given in Table 1. For pyrene-PMMA 1.02 g (10.2 mmol) methyl methacrylate, 107.2 mg (0.2 mmol) RAFT agent and 8 mg (4.9×10^{-5} mol) AIBN were used. After precipitation, 997 mg (97 %) rose colored polymer powder was collected. δ_{H} (100 MHz; CDCl_3 ; Me_4Si) 3.54 (3H, s, O- CH_3), 1.84 (2H, m, CH_2), 0.96 (1H, s, CH), 0.80 (3H, m, CH_3). For pyrene-PDEGMEMA 1.08 g (5.8 mmol) (diethylene glycol monomethyl ether) methacrylate ((2-methoxy-ethoxy)-ethyl methacrylate) and 1.2 mg (7.2×10^{-6} mol) AIBN were used. After precipitation, 886 mg (82%) rose colored jelly polymer was collected. δ_{H} (100 MHz; CDCl_3 ; Me_4Si) 4.4–3.5 (4d, 8H, $-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_3$), 3.3 (s, 3H, $-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_3$), 2.0–1.6 (m, 2H, $[-\text{CH}_2-\text{CRCH}_3-]_n$), 1.3–0.7 (m, 3H, $[-\text{CH}_2-\text{CR}(\text{CH}_3)-]_n$).

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