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Tunable thermoresponsive water-dispersed multiwalled carbon nanotubes†

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Received (in Cambridge, UK) 23rd November 2007, Accepted 11th January 2008
First published as an Advance Article on the web 1st February 2008
DOI: 10.1039/b718112d

Polymers containing poly(ethylene glycol) methacrylate and 2-(2-methoxyethoxy)ethyl methacrylate have been synthesized by Cu(0)-mediated radical polymerisation for use as thermo-responsive water-dispersants for carbon nanotubes.

Poly(ethylene glycol) (PEG) is an inexpensive, non-charged, water-soluble, biocompatible polymer and has recently raised interest in terms of being both thermo-responsive and water-soluble.[1–3] Lutz *et al.* reported that copolymers with tunable lower critical solution temperature LCST (26–90 °C) could be obtained by changing the ratio of the long chain-length poly(monomethoxy-ethylene glycol) methacrylate (PEGMA) and shorter chain-length 2-(2-methoxyethoxy)ethyl methacrylate (DEGMA).[1,3]

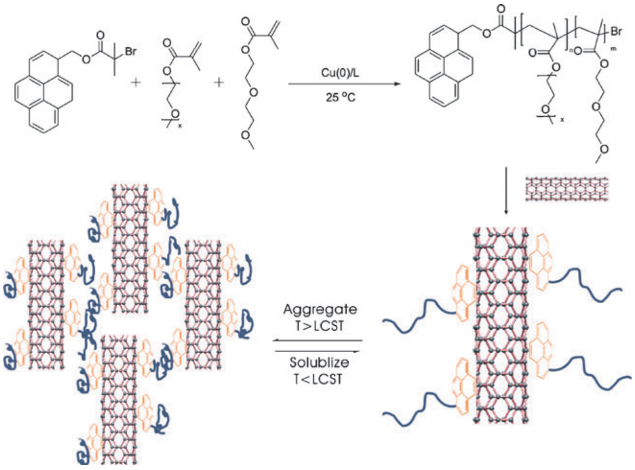
Copper(I) medicated living radical polymerisation is an excellent method to prepare well-defined polymers.[4,5] This has been extended to the use of Cu(II) salts in combination with reducing agents.[6,7] Recently, Percec *et al.* have reported on the use of Cu(0) in a "single-electron transfer (SET)" living polymerization".[8,9] This uses zero-valent copper powder/wire as the catalyst, in polar solvents and in the presence of certain N-ligands under very mild reaction conditions, at ambient temperature. This can use a small amount of catalyst and generate polymers with high molecular weight with ultra-fast rates.

We rationalized that polymerisation of PEGMA should be favourable in non polar/coordinating solvents without additional polar solvent due to the excellent coordination attributes of the oxyethylene groups from PEG. Thus, we report on the homo(co)polymerization of PEGMA and DEGMA using a pyrene containing initiator in conjunction with a Cu(0)/Me_6Tren catalytic system. Pyrene-containing polymers are often used for non-covalent modification of carbon nanotubes in a nondestructive strategy,[10–14] we might then make water-dispersible carbon nanotubes.[15–21] Through this non-covalent side-wall functionalization strategy, the pyrene-functionalised polymers synthesised were used to modify carbon nanotubes and thus thermosensitive water-dispersible carbon nanotubes were prepared. (Scheme 1). Surface-grafted Poly(NIPAM) has also been demonstrated to form thermo-responsive MWNT dispersions.[22,23]

Homopolymers and copolymers of $PEGMA_{475}$ (PEGMA with M_n = 475 g mol^{-1}) and DEGMA with pyrene-terminal functionality were obtained using a copper(0) powder/Me_6Tren catalytic system at 25 °C, Table 1. This form of controlled radical polymerisation enables α-functional polymers to be prepared from easily prepared functional initiators. The polydispersity index and the control of molecular weight is less important in the current case.[4,5]

The first-order kinetic plots for the copolymerisation of PEGMA and DEGMA is linear and as the conversion increases the M_n of the copolymer increases, although the PDi is relatively high (~1.5) (Fig. 1).

Within 6 h at 25 °C, a conversion of >90% was obtained. A similar behavior was observed for the homopolymerisation of both monomers. ^{1}H NMR of the polymers confirmed the presence of the pyrene end-functionality. The pyrene group also facilitates measurement of M_n by NMR, which are all close to the theoretical values, although the value from SEC is higher (Table 1). Integrations were carried out three times in each case with errors of less than 3% observed, in all cases, between measured values (see ESI†). All of the data indicated that both ethylene glycol-containing monomers favour polymerisation mediated by Cu(0) without the addition of polar solvents with a fast polymerisation rate obtained at ambient temperature. Lower critical solution temperatures (cloud points, LCSTs) of the polymers were measured (Table 1), allowing a tunable LCST between 29 and 91 °C by modification of the copolymer composition. If we assume LCST would follow the same relationship as T_g for copolymers then for this composition we would predict an LCST of approximately 41 °C. All three polymers showed reversible noncovalent



Scheme 1 Synthesis of pyrene-terminal polymers by using Cu(0) as the source of metal catalyst and preparation of thermosensitive water-soluble carbon nanotube conjugates.

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† Electronic supplementary information (ESI) available: Full experimental details, H NMR spectra and kinetic plots. See DOI: 10.1039/b718112d

Table 1 Summary of molecular characteristics of the polymers synthesized in this work

	Composition[a] (PEGMA : DEGMA)	$M_{n,\mathrm{SEC}}$[b]	$M_{n,\mathrm{NMR}}$[c]	$M_{n,\mathrm{th}}$[d]	PDi[b]	LCST[e]/°C
1	0 : 100	32 300	20 700	19 200	1.21	29
2	10 : 90	32 600	21 500	22 100	1.53	45
3	100 : 0	60 100	49 100	47 900	1.75	91

[a] Initial molar ratio of monomers. [b] Measured by SEC in THF, with PMMA standards. [c] Determined by ^{1}H NMR in $CDCl_3$. [d] Calculated using equation $M_{\mathrm{n,th}} = (\mathrm{DP} \times M_{\mathrm{W_m}}) + M_{\mathrm{W_i}}$, where DP is 100, $M_{\mathrm{W_m}}$ is the (average) molecular weight of (co)momomer and $M_{\mathrm{W_i}}$ is the molecular weight of initiator. [e] Measured on a Varian Cary 100 UV-Vis spectrophotometer with temperature control.

dispersion of multi-walled carbon nanotubes (MWNT) in water *via* side-wall functionalization. In the case of polymer **2** an $R_{\mathrm{initial}} = 5$ was used for stabilization following reports that the ratio of polymer to CNTs wt (R_{initial}) must be >2 for stable dispersions using pyrene-containing polymers.[11] After a short sonication period, a stable dispersion of MWNTs was observed, (Fig. 2(B)), when this solution was heated above the LCST of the polymer (60 °C), the solution became cloudy and the MWNTs aggregated and precipitated (Fig. 2(C)). After cooling the vial to a temperature < LCST of polymer **2**, the MWNTs were redispersed with additional agitation, this was typical for all polymers. However, it is noted that in the case of polymer **3** the LCST was close enough to the boiling point to render the experiment difficult. The modified MWNTs were recovered by centrifugation and washed with water several times in order to eliminate the excess of pyrene-containing copolymer. The recovered polymer-modified MWNTs formed stable dispersions in water at ambient temperature confirming that π–π stacking results in the strong adsorption of pyrene moiety with MWNT. The grafting ratio (GR), defined as the mass ratio of grafted polymer to nanotubes, was estimated by TGA and found to be in the range = 0.35–0.45. The MWNT–**2** solution was also examined by UV-Vis spectrophotometry (670 nm) after dilution to 0.05 mg mL^{-1} (Fig. 2(A)) and the same pattern was observed as for the neat polymer **2** solution with a slight shift to higher temperature. In addition, the absorbance of MWNT–**2** was >0 even at the start of the measurement due to the presence of MWNTs in the solution, as the polymer solution was set with Abs = 0. TEM further confirmed the successful adsorption of the pyrene-functional polymers onto carbon nanotubes, as a clear polymer layer could be observed around the MWNT (Fig. 2(D)).

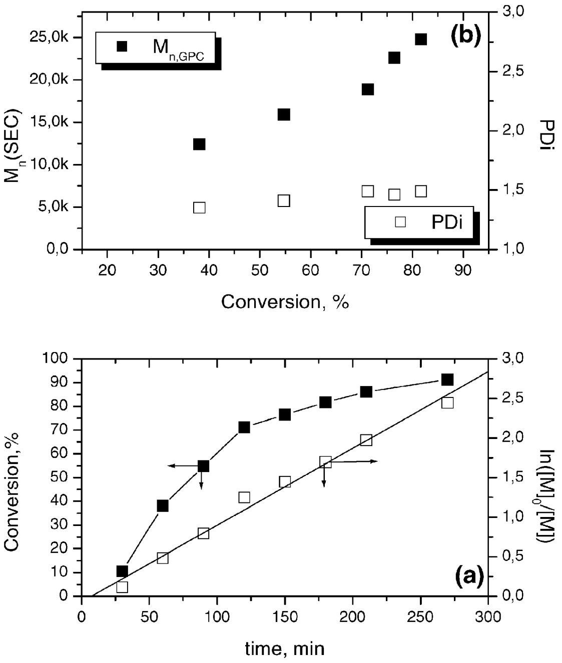

Fig. 1 (a) Conversion *vs.* time and semilogarithmic kinetic curves and (b) M_n, PDi *vs.* conv. curves for copolymerisation of PEGMA and DEGMA. $[\mathrm{PEGMA}]_0 : [\mathrm{initiator}]_0 : [\mathrm{Cu(0)\ powder}]_0 : [\mathrm{ligand}]_0 = 100 : 1 : 1 : 1$ in toluene (50 wt%), conversion measured relative to mesitylene internal standard by ^{1}H NMR.

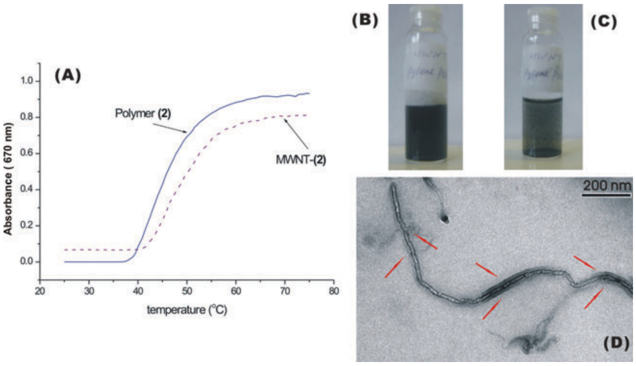

Fig. 2 (A) Absorbance (670 nm) as a function of temperature for aqueous dispersions (3 mg mL^{-1}) of polymer **2** (solid line) and polymer **2**-modified MWNTs (dashed line); (B) Polymer **2**-modified MWNTs dispersed in water at ambient temperature and (C) after heating at 60 °C; (D) TEM of the polymer **2**-MWNTs conjugate.

In summary, polymerisation of PEGMA and DEGMA has been successfully carried out using a Cu(0)/Me_6Tren catalyst system and a pyrene initiator at 25 °C in toluene. Pyrene-terminal polymers with tunable LCSTs have been prepared and used to for the thermosensitive water-dispersion of MWNTs.

Notes and references

1 J. F. Lutz, O. Akdemir and A. Hoth, *J. Am. Chem. Soc.*, 2006, **128**, 13046–13047.
2 S. Han, M. Hagiwara and T. Ishizone, *Macromolecules*, 2003, **36**, 8312–8319.
3 K. L. Robinson, M. V. de Paz-Banez and S. P. Armes, *Macromolecules*, 2001, **34**, 5799–5805.
4 M. Kamigaito, T. Ando and M. Sawamoto, *Chem. Rev.*, 2001, **101**, 3689–3745.
5 A. Limer and D. M. Haddleton, *Prog. React.-Kinet. Mech.*, 2004, **29**, 187–241.
6 A. de Vries, B. Klumperman, D. de Wet-Roos and R. D. Sanderson, *Macromol. Chem. Phys.*, 2001, **202**, 1645–1648.

7 K. Min, H. Gao and K. Matyjaszewski, *J. Am. Chem. Soc*., 2005, **127**, 3825–3830.

8 V. Percec, A. V. Popov, E. Ramirez-Castillo, M. Monteiro, B. Barboiu, O. Weichold, A. D. Asandei and C. M. Mitchell, *J. Am. Chem. Soc*., 2002, **124**, 4940–4941.

9 V. Percec, T. Guliashvili, J. S. Ladislaw, A. Wistrand, A. Stjerndahl, M. J. Sienkowska, M. J. Monteiro and S. Sahoo, *J. Am. Chem. Soc*., 2006, **128**, 14156–14165.

10 R. J. Chen, Y. Zhang, D. Wang and H. Dai, *J. Am. Chem. Soc*., 2001, **123**, 3838–3839.

11 P. Petrov, F. Stassin, C. Pagnoulle and R. Jerome, *Chem. Commun*., 2003, 2904–2905.

12 F. J. Gomez, R. J. Chen, D. Wang, R. M. Waymouth and H. Dai, *Chem. Commun*., 2003, 190–191.

13 N. Nakashima, Y. Tomonari and H. Murakami, *Chem. Lett*., 2002, 638–639.

14 X. Lou, R. Daussin, S. Cuenot, A. S. Duwez, C. Pagnoulle, C. Detrembleur, C. Bailly and R. Jerome, *Chem. Mater*., 2004, **16**, 4005–4011.

15 M. J. O'Connell, P. Boul, L. M. Ericson, C. Huffman, Y. Wang, E. Haroz, C. Kuper, J. Tour, K. D. Ausman and R. E. Smalley, *Chem. Phys. Lett*., 2001, **342**, 265–271.

16 F. Pompeo and D. E. Resasco, *Nano Lett*., 2002, **2**, 369–373.

17 V. Georgakilas, N. Tagmatarchis, D. Pantarotto, A. Bianco, J. P. Briand and M. Prato, *Chem. Commun*., 2002, 3050–3051.

18 A. Star, D. W. Steuerman, J. R. Heath and J. F. Stoddart, *Angew. Chem., Int. Ed*., 2002, **41**, 2508–2512.

19 H. Dodziuk, A. Ejchart, W. Anczewski, H. Ueda, E. Krinichnaya, G. Dolgonos and W. Kutner, *Chem. Commun*., 2003, 986–987.

20 W. Huang, S. Taylor, K. Fu, Y. Lin, D. Zhang, T. W. Hanks, A. M. Rao and Y. P. Sun, *Nano Lett*., 2002, **2**, 311–314.

21 L. Tao, G. Chen, G. Mantovani, S. York and D. M. Haddleton, *Chem. Commun*., 2006, 4949–4951.

22 G. Y. Xu, W. T. Wu, Y. S. Wang, W. M. Pang, P. H. Wang, G. R. Zhu and F. Lu, *Nanotechnology*, 2006, **17**, 2458–2465.

23 C. Y. Hong, Y. Z. You and C. Y. Pan, *Chem. Mater*., 2005, **17**, 2247–2254.