Polymer 53 (2012) 2008-2014

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Extraordinary aspects of bromo-functionalized multi-walled carbon nanotubes as initiator for polymerization of ionic liquid monomers

Yu-Hsun Chang^a, Pei-Yi Lin^b, Ming-Sung Wu^b, King-Fu Lin^{a,b,*}

^a Institute of Polymer Science and Engineering, National Taiwan University, Taipei 106, Taiwan ^b Department of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan

ARTICLE INFO

Article history: Received 2 December 2011 Received in revised form 21 February 2012 Accepted 8 March 2012 Available online 15 March 2012

Keywords: Carbon nanotube ATRP Ionic liquid

ABSTRACT

Two ionic liquid monomers, 1-(2-acryloyloxy-ethyl)-3-methyl-imidazol-1-ium iodide (AMImI) and 1-(2-acryloyloxy-ethyl)-3-methyl-benzoimidazol-1-ium iodide (AMBImI), were synthesized and polymerized through atom transfer radical polymerization (ATRP). Poly(AMImI)-grafted multi-walled carbon nanotubes (denoted as MWCNT-poly(AMImI)) could also be fabricated through "grafting from" method of ATRP using bromo-functionalized MWCNT (denoted as MWCNT–Br) as initiator but MWCNT-poly(AMBImI) could not. Based on the thermogravimetric analysis and high resolution transmission electron microscopy, AMBImI monomer has encapsulated the MWCNT–Br probably through the π - π and cation- π interactions invalidating the initiation capability of MWCNT–Br. Besides, by mixing AMBImI with MWCNT–Br directly at room temperature, the MWCNT–Br was coated with a thin layer of AMBImI, whereas MWCNT–Br could not physisorb AMImI. Both MWCNT-poly(AMImI) and AMBImI-encapsulated MWCNT were dispersed well in 1-methyl-3-propylimidazolium iodide ionic liquid.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Multi-walled carbon nanotubes (MWCNT) possess excellent mechanical, electrical, and thermal properties [1]. It has tremendous potential applications in composites [2-5], electrodes [6-8], sensors [9,10], and electrolytes [11,12]. Researchers usually oxidized the sidewall of MWCNT with nitric acid and/or sulfuric acid [13] to increase its dispersion in polar solvent and polymer matrix. Ionic liquid, a molten salt with low melting point at ambient temperature, has recently attracted great attention owing to its zero volatility, superior electrochemical properties and high ionic conductivity [14,15]. It has wide range of applications, especially in catalysis [15], sensors [16], solar cells [17], and so on. To combine the superior ionic conductivity of ionic liquid with high electric conductivity of MWCNT, researchers have incorporated the MWCNT with the ionic liquid through chemical reactions [18–22] or physical interactions [23-25]. However, to the best of our knowledge, few researchers attempted to graft the ionic liquid polymer onto MWCNT.

Atom transfer radical polymerization (ATRP) has been demonstrated to be a powerful living radical polymerization tool for grafting the functional polymer to MWCNT [26–28] and other substrates [29,30]. The ionic liquid monomer could also be polymerized through ATRP [31,32], by which the poly(ionic liquid) has been reported to graft on silicon wafer forming the so-called poly(ionic liquid) brushes [31]. Therefore, we considered that by choosing proper ionic liquid monomer we would be able to fabricate the poly(ionic liquid)-grafted MWCNT through "grafting from" method of ATRP.

Accordingly, in this work we synthesized two types of ionic liquid monomers, 1-(2-acryloyloxy-ethyl)-3-methyl-imidazol-1ium iodide (AMImI) and 1-(2-acryloyloxy-ethyl)-3-methyl-benzoimidazol-1-ium iodide (AMBImI), which were then polymerized through ATRP. Poly(AMImI)-grafted MWCNT (denoted as MWCNTpoly(AMImI)) could be fabricated through "grafting from" method of ATRP but poly(AMBImI)-grafted MWCNT could not, because AMBImI tended to encapsulate the bromo-functionalized MWCNT (denoted as MWCNT–Br) probably through the π – π [33] and cation $-\pi$ interactions [34] invalidating the initiation capability of MWCNT-Br. By directly mixing AMBImI with MWCNT-Br, MWCNT were coated with a thin layer of AMBImI (denoted as MWCNT-Br/ AMBImI) but on the contrary MWCNT-Br/AMImI could not be fabricated. Both MWCNT-poly(AMImI) and AMBImI-encapsulated MWCNT were dispersed well in 1-methyl-3-propylimidazolium iodide (PMII), which is a typical ionic liquid used for quasi-solid state dye-sensitized solar cells [35,36]. Our preliminary study showed that by addition of 0.05 wt% MWCNT-poly(AMImI) to PMII





^{*} Corresponding author. Institute of Polymer Science and Engineering, National Taiwan University, Taipei 106, Taiwan. Tel.: +886 2 3366 1315; fax: +886 2 2363 4562.

E-mail address: kflin@ntu.edu.tw (K.-F. Lin).

^{0032-3861/\$ –} see front matter @ 2012 Elsevier Ltd. All rights reserved. doi:10.1016/j.polymer.2012.03.020

electrolyte system, the power conversion efficiency (PCE) of fabricated DSSC was mildly increased from 5.03 to 5.59% [37]. However, as poly(AMImI) was used as a quasi-solid solvent for the electrolyte system, the addition of 0.5 wt% MWCNT/AMBImI significantly increased the PCE from 1.16 to 3.55%.

2. Experimental section

2.1. Materials

MWCNT of >90% carbon basis, 10–30 nm o.d., 2–10 nm i.d., and 0.1–10 μ m length was purchased from Aldrich. All chemicals were purchased from Arcos and Aldrich except acryloyl chloride (Alfa Aesar) and thionyl chloride (Riesel-deHaën). Tetrahydrofuran (THF) and dichloromethane were distilled over CaH₂ and sodium prior to use.

2.2. Characterization

¹H NMR Spectra were recorded on a Bruker Avance-500 MHz FT NMR at room temperature using D-DMSO as solvent. Thermogravimetric analysis (TGA) was conducted using TA Instruments SDT-Q600 at a heating rate of 10 °C/min under N₂. X-ray photoelectron spectroscopy (XPS) was conducted using PHI 5000 Versaprobe ULVAC-PHI and the background pressure in analysis chamber was controlled at 10^{-5} Pa. High resolution transmission electron microscopy (HR-TEM) investigation was conducted using a Philip Tecnai G² LaB6 Gun Transmission Electron Microscope with Gatan Dual Vision CCD Camera.

2.3. Preparation of 2-iodoethylacrylate

2-lodoethanol (11.3 mmol, 4.3 mL) and acryloyl chloride (46.4 mmol, 4.7 mL) were mixed in 50 mL dichloromethane and then added with triethylamine (12 mL). The mixture was reacted at 0 °C with stirring for 6 h in argon (Ar) atmosphere. After the reaction mixture was filtrated to remove the precipitate and washed with

100 mL water several times, the organic layer was dried over MgSO₄ and the solvent was removed under reduced pressure to afford the solid product. Yield: 7.8 g (57%). ¹H NMR (500 MHz, CDCl₃, δ /ppm): 3.27(t,2H), 4.33(t,2H), 5.81(dd,1H), 6.08(dd,1H), 6.41(dd,1H).

2.4. Synthesis of AMImI

1-Methylimidazole (31 mmol) and 2-iodoethylacrylate (31 mmol) were dissolved in 50 mL acetonitrile and reacted at 85 °C under reflux for 3 days. After the solvent was removed and trace amount of water was added to dissolve the raw product, it was purified by washing with dichloromethane several times and drying under reduced pressure. Yield: 6.6 g (62%). ¹H NMR(500 MHz, D-DMSO, δ /ppm): 3.94(s,3H), 4.56(t,2H), 4.62(t,2H), 6.08(dd,1H), 6.26(dd,1H), 6.42(dd,1H), 7.88(t,1H), 7.90(t,1H), 9.28(s,1H).

2.5. Synthesis of AMBImI

Synthesis procedure of AMBImI is similar to that of AMImI except that 1-methylimidazole was replaced by 1-methylbenzimidazole. Yield: 2.8 g (25%). ¹H NMR(500 MHz, D-DMSO, δ /ppm): 4.11(s,3H), 4.55(t,2H), 4.87(t,2H), 5.93(dd,1H), 6.07(dd,1H), 6.23(dd,1H), 7.70(dd,2H), 8.08(dd,1H), 8.20(dd,1H), 9.80(s,1H).

2.6. Polymerization of AMImI and AMBImI through ATRP

CuBr (0.065 mmol), pentamethyldiethylenetriamine (PMDETA, 0.130 mmol) and ionic liquid monomer (6.5 mmol) were placed into a 25 mL round-bottom flask which had been loaded with 10 mL DMF and purged with dry Ar for 30 min. The mixture was purged with Ar for another 20 min and then ethyl 2-bromoisobutyrate (0.065 mmol) initiator was added to the flask. The resulting solution was degassed with freeze-pump-thaw process three times and then reacted at 90 °C for 1 day. The raw product was diluted with 10 mL DMF and precipitated with large amount of acetone. By repeating the dissolution-precipitation process three times to



AMBImI

Fig. 1. Scheme of synthesis for (a) AMImI and (b) AMBImI.



Fig. 2. ¹H NMR spectra of (a) AMImI and (b) AMBImI.

remove the non-reacted monomer, the product was filtrated and dried under reduced pressure. The yield of poly(AMImI) and poly(AMBImI) was 1.0 g (50%) and 0.8 g (40%).

2.7. Preparation of MWCNT–Br

MWCNT–Br was prepared according to the literature [38,39]. In general, MWCNT was oxidized by 65% HNO₃ first and then reacted with thionyl chloride to afford MWCNT–C(==O)Cl. MWCNT–C(==O)–OC₂H₄OH (denoted as MWCNT–OH) was prepared by



Fig. 3. Reaction scheme of ATRP to prepare poly(AMIml) and poly(AMBIml) using ethyl 2-bromoisobutyrate as an initiator.

by reaction of MWCNT-OH with 2-bromo-2-methylpropionyl bromide. а DMS poly(AMImI) H₂C d DMF 0110 100 1 88 24.64) 18 -5 ò 7 4 3 1 ppm 9 8 6 2 b H2D DMSO poly(AMBImI)

reaction of MWCNT-C(=0)-Cl with glycol. MWCNT-C(=0)-

OC₂H₄OC(=O)-C₃H₆Br (denoted as MWCNT-Br) was prepared



Fig. 4. ¹H NMR spectra of (a) poly(AMImI) and (b) poly(AMBImI).



Fig. 5. Schemes of synthesis to prepare (a) MWCNT–Br, and (b) MWCNT- poly(AMImI) and expected MWCNT-poly(AMBImI).

2.8. Preparation of MWCNT-poly(AMImI) and expected MWCNT-poly(AMBImI)

CuBr (9.3 mg, 0.065 mmol), PMDETA (22.5 mg, 0.130 mmol), and respective ionic liquid monomers (6.5 mmol) to prepare MWCNT-poly(AMImI) and expected MWCNT-poly(AMBImI) were placed into a 25 mL round-bottom flask which had been loaded with 10 mL Ar-purged DMF. The solutions after purging with Ar for 20 min were added with MWCNT–Br (0.1 g) and then placed in an ultrasonic bath for another 20 min. The resulting solutions were degassed with freeze-pump-thaw process three times and then reacted at 90 °C for 1 day. The mixtures were poured into large volume of acetone and filtrated through a 0.22 μ m PVDF membrane to remove the liquid filtrate. After repeatedly washing the solid retentates with acetone and drying under reduced pressure, MWCNT-poly(AMImI) and expected MWCNT-poly(AMBImI) in powder form were obtained.

2.9. Preparation of 1-methyl-3-propylimidazolium iodide (PMII)

1-Methylimidazole (0.32 mol) and 1-iodopropane (0.32 mol) were dissolved in 320 mL of dried THF and stirred at room



Fig. 6. TGA thermograms of pristine MWCNT, MWCNT-OH, MWCNT-Br, MWCNTpoly(AMIml), expected MWCNT-poly(AMBIml), MWCNT-Br/AMIml, MWCNT-Br/ AMBIml, poly(AMIml), and poly(AMBIml).

temperature for 3 days. The yellow layer formed at the bottom was collected and washed with ethyl acetate (EA) to remove unreacted materials. After washing with EA several times, it was filtrated through 0.45 μ m PVDF membrane to obtain the product. ¹H NMR (500 MHz, CDCl₃, δ /ppm): 0.87(t,3H), 1.86(m,2H), 4.02(s,3H) 4.19(t,2H), 7.52(d,1H), 7.56(d,1H), 9.79(s,1H).

3. Results and discussion

The detailed synthesis scheme for AMImI and AMBImI monomers is illustrated in Fig. 1. Their chemical structures with the assigned proton peaks in the ¹H NMR spectra are shown in Fig. 2. The vinyl peaks of AMImI and AMBImI can be clearly seen in between 5 and 7 ppm. Both of ionic liquid monomers were then polymerized through ATRP according to the scheme illustrated in Fig. 3 using CuBr as a catalyst and PMDETA as a ligand. The NMR spectra of poly(AMImI) and poly(AMBImI) shown in Fig. 4 revealed that the vinyl groups have been reacted and all other proton peaks broadened. From the NMR spectra, the number average molecular weight of poly(AMImI) can be estimated as 3704 g/mol (~12 monomer repeating units) determined by dividing the integrals of alkyl proton peaks (H_{b.c.d}) by the initiator proton peak (H_a). By the same token, the number average molecular weight of poly(AMBImI) is estimated as 7876 g/mol (~22 repeating units). The reason behind the substantially higher molecular weight of poly(AMBImI) than that of poly(AMImI) is not clear. However, it might be due to the additional aromatic ring for AMBImI monomer to induce the $\pi-\pi$ [33] and cation $-\pi$ [34] interactions between monomers increasing their chance for polymerization.

MWCNT-poly(AMImI) and expected MWCNT-poly(AMBImI) were prepared according to the schemes illustrated in Fig. 5. In the beginning, MWCNT was oxidized by HNO₃ and then reacted with thionyl chloride to produce MWCNT–C(=O)–Cl. MWCNT–OH with -C(=O)– OC_2H_4 – linkage was prepared by reaction of

Table 1

Molecular weights of poly(AMImI), poly(AMBImI), and their respective polymers for MWCNT-poly(AMImI) and expected MWCNT-poly(AMBIMI).

	poly(AMImI)	poly(AMBImI)	MWCNT-poly(AMImI)	MWCNT-poly(AMBImI)
	(NMR)	(NMR)	(TGA)	(TGA)
Mn (g/mole)	3704	7876	3383	709
Xn	12	22	11	2

MWCNT-C(==O)-Cl with glycol, whereas MWCNT-Br with -C(==O)-OC₂H₄OC(=O)-C₃H₆- linkage was prepared by reaction of MWCNT-OH with 2-bromo-2-methylpropionyl bromide (see Fig. 5a).

MWCNT–Br was then used as an initiator to polymerize AMIMI, by which poly(AMIMI) grafted on MWCNT to form MWCNTpoly(AMIMI). Interestingly, by using the same procedure MWCNT–Br has a problem to polymerize AMBIMI, which will be discussed below on the basis of TGA results.

The degree of polymerization for poly(AMImI) and expected poly(AMBImI) grafting from MWCNT–Br can be calculated from their TGA data shown in Fig. 6 [39]. By taking the remaining

weight at 800 °C, MWCNT–OH has 7.54% weight loss which is related to the weight of $-C(=O)-OC_2H_4-OH$ groups ((W_{OH}, based on per gram of MWCNT–OH)) and MWCNT–Br has 16.3% weight loss related to the weight of $-C(=O)-OC_2H_4OC(=O)-C_3H_6$ –Br groups (W_{Br}, based on per gram of MWCNT–Br). From Fig. 5a, we can estimate the initiator groups per gram of MWCNT–Br and per gram of MWCNT as follows. Assuming that the weight of total $-C(=O)-C_3H_6Br$ groups per gram of MWCNT–Br in the enclosed region shown in Fig. 5a is X, it can be calculated by $[W_{Br} - W_{OH}(1 - X)] = X$, by which X = 0.0947 g was obtained. Therefore, total initiator groups per gram of MWCNT–Br is calculated by X/Mw = 0.636 mmol, where Mw = 149 is the



Fig. 7. HR-TEM micrographs of (a-b) pristine MWCNT, (c-d) MWCNT-poly(AMImI) and (e-f) expected MWCNT-poly(AMBImI).

molecular weight of $-C(=O)-C_3H_6Br$ groups subtracting a proton. It can be converted to 0.76 mmol initiator groups per gram of MWCNT by $0.636/(1 - W_{Br}) = 0.76$. Therefore, based on the TGA results, we can estimate the number average molecular weight of 3383 g/mol for poly(AMImI) and 709 g/mol for poly(AMBImI) grafting to MWCNT. All molecular weights of poly(ionic liquid) and grafting poly(ionic liquid) on MWCNT are summarized in Table 1. Notably, although the MWCNT/ionic liquid hybrids have been studied extensively recently [18–25], to polymerize ionic liquid monomers directly on MWCNT using MWCNT–Br as an initiator for ATRP in this work was the first attempt in the literature.

Molecular weight of the grafting poly(AMImI) on MWCNT is slightly lower than that of neat poly(AMImI), which is reasonable because the initiator was chemically bound on MWCNT. However, it was surprising to find such low degree of polymerization (Xn = 2) for poly(AMBImI) grafting on MWCNT. TGA results showed that MWCNT-poly(AMImI) and poly(AMImI) have similar decomposition temperature of 275 °C at 5% weight loss. Whereas the decomposition temperature of expected MWCNTpoly(AMBImI) at 251 °C is lower than that of neat poly (AMBImI) (285 °C), implying that AMBImI monomer did not polymerize on the surface of MWCNT-Br. Instead, it might be physisorbed on the surface of MWCNT-Br invalidating its initiation capability. To verify our presumption, we mixed MWCNT-Br and AMBImI together in DMF solvent for one day at room temperature without addition of any ligand and catalyst. and then washed the mixed slurry solution with large amount of acetone and drving. The final product of MWCNT-Br/AMBImI was subjected to the TGA measurement. Interestingly, the TGA plot of MWCNT-Br/AMBImI almost overlaps with that of expected MWCNT-poly(AMBImI) except for the initial degradation region, indicating that AMBImI molecules indeed physisorbed onto the MWCNT-Br.

On the contrary, the weight loss at 800 °C for MWCNT-Br/ AMImI prepared by the procedure similar to the MWCNT-Br/ AMBImI is almost the same as that of MWCNT-Br, suggesting that MWCNT-Br can not physisorb AMImI simply by mixing. Hence, it is possible to assume that due to the additional aromatic ring possessed by AMBImI compared to AMImI, AMBImI-encapsulated MWCNT–Br by $\pi - \pi$ [33] and cation– π [34] interactions invalidating the initiation capability of MWCNT-Br, but AMImI can not. It has been reported that MWCNT is able to physisorb the imidazole-based ionic liquid through π -electronic interaction [24,40]. Fujigaya et al. [41] also reported that polybenzimidazole can encapsulate MWCNT by $\pi - \pi$ interaction. Notably, Sainsbury et al. [42] have developed a theory to predict the coverage of tetraoctylammonium bromide-stabilized gold nanoparticles on alkyl and alkylthiolmodified MWCNTs based on their covalent bonding and noncovalent interaction energy.

The skin of MWCNT observed by HR-TEM shows a clean and smooth multi-layer structure as illustrated in Fig. 7(a) and (b), by which the wall thickness and outer diameter of MWCNT were measured as 5 and 14.6 nm. The HR-TEM micrographs of MWCNT-poly(AMImI) show an amorphous layer of poly(AMImI) with ~27 nm thickness coating on the outer surface of MWCNT (see Fig. 7(c) and (d)). As to the expected MWCNT-poly(AMBIMI), ~2 nm of AMBIMI amorphous layer was coated on the surface of MWCNT (see Fig. 7(e) and (f)), much thinner than poly(AMImI) layer on MWCNT-poly(AMImI). These morphologies supported the TGA results shown in Fig. 6.

To further verify the presence of poly(AMIMI) grafting on MWCNT and AMBIMI coating on MWCNT, we used XPS to analyze their atomic structures. The XPS full-scan spectra and core-level



Fig. 8. XPS full-scan spectra of (a) MWCNT-poly(AMImI) and (b) expected MWCNT-poly(AMBImI). Insets were their I_{3d} and N_{1s} core-level spectra.

spectra of MWCNT-poly(AMImI) and expected MWCNT-poly(AMBImI) are shown in Fig. 8. The appearance of I_{3d} (618 eV) and N_{1s} (401 eV) contributed by the imidazole and benzimidazole iodide indicated the presence of ionic liquids on MWCNT. By



Fig. 9. Photographs of PMII and its mixed solutions with pristine MWCNT, MWCNTpoly(AMImI), and expected MWCNT-poly(AMBImI).

normalizing the C_{1s} peaks to the same height for both samples in their XPS spectra, we can find that the contents of O_{1s} , N_{1s} and I_{3d} elements for MWCNT-poly(AMIMI) are much higher than those for expected MWCNT-poly(AMBIMI), which also supported their TGA results.

Finally, all the MWCNT samples were dispersed in the PMII ionic liquid, which is often used as a non-volatile solvent for dyesensitized solar cells (DSSC) due to its low viscosity [35]. After standing for a week, the pristine MWCNT in PMII tended to aggregate and adhere on the wall of the vial as revealed by the photograph shown in Fig. 9. Interestingly, both MWCNT-poly(AMImI) and expected MWCNT-poly(AMBImI) showed well dispersed in PMII (1 mg MWCNT in 3 mL PMII). Because MWCNT has superior electric conductivity, we expect that MWCNT-poly(AMImI) and expected MWCNT-poly(AMBImI) would have a great potential to apply for ionic liquid-based DSSC to enhance the photovoltaic performance.

4. Conclusions

Number average molecular weights of poly(AMImI) and poly (AMBImI) polymerized by ATRP were 3704 and 7876 g/mol as determined by ¹H NMR. The higher molecular weight for poly (AMBImI) was attributed to its additional aromatic ring inducing the $\pi-\pi$ and cation— π interactions between the monomers. MWCNT-poly(AMImI) can also be fabricated through "grafting from" method of ATRP using MWCNT—Br as an initiator. The number average molecular weight of poly(AMImI) grafting on MWCNT was 3383 g/mol as estimated by TGA data. Based on the TGA and HR-TEM analysis, MWCNT—Br physisorbed a thin layer of AMBImI invalidating the initiation capability of MWCNT—Br.

Acknowledgment

The authors acknowledge the financial support of the National Science Council in Taiwan, Republic of China, through Grant NSC 96-2221-E-002-144-MY3.

References

- [1] lijima S. Nature 1991;354:56-8.
- [2] Liu YL, Chang YH, Liang M. Polymer 2008;49:5405–9.
- [3] Kuila BK, Malik S, Batabyal SK, Nandi AK. Macromolecules 2007;40:278-87.

- [4] Grossiord N, Loos J, Laake LV, Maugey M, Zakri C, Koning CE, et al. Adv Funct Mater 2008;18:3226–34.
- [5] Chang CM, Liu YL. Carbon 2010;48:1289-97.
- [6] Lee WJ, Ramasamy E, Lee DY, Song JS. Sol Energy Mater Sol Cells 2008;92: 814–8.
- [7] Huang KC, Wang YC, Dong RX, Tsai WC, Tsai KW, Wang CC, et al. J Mater Chem 2010;20:4067-73.
- [8] Kim TA, Kim HS, Lee SS, Park M. Carbon 2012;50:444-9.
- [9] Nossol E, Zarbin AJG. Adv Funct Mater 2009;19:3980-6.
- [10] Wu Z, Feng W, Feng Y, Liu Q, Xu X, Sekino T, et al. Carbon 2007;45: 1212-8.
- [11] Seo SH, Kim SY, Koo BK, Cha SI, Lee DY. Langmuir 2010;26:10341-6.
- [12] Huang KC, Chang YH, Chen CY, Liu CY, Lin LY, Vittal R, et al. J Mater Chem 2011;21:18467-74.
- [13] Rosca ID, Watari F, Uo M, Akasaka T. Carbon 2005;43:3124-31.
- [14] Yu B, Zhou F, Wang C, Liu W. Eur Polym J 2007;43:2699-707.
- [15] Rantwijk FV, Sheldon RA. Chem Rev 2007;107:2757-85.
- [16] Fukushima T, Asaka K, Kosaka A, Aida T. Angew Chem Int Ed 2005;44:2410–3.
 [17] Wei D, Unalan HE, Han D, Zhang O, Niu L, Amaratunga G, et al. Nanotechnology 2008:19:424006.
- [18] Wang B, Wang X, Lou W, Hao J. J Phys Chem C 2010;114:8749-54.
- [19] Hong SH, Tung TT, Trang LKH, Kim TY, Suh KS. Colloid Polym Sci 2010;288: 1013-8.
- [20] Park MJ, Lee JK, Lee BS, Lee YW, Choi IS, Lee SG. Chem Mater 2006;18: 1546–51.
- [21] Yu B, Zhou F, Liu G, Liang Y, Huck WTS, Liu W. Chem Commun; 2006:2356-8.
- [22] Wang Z, Zhang O, Kuehner D, Xu X, Ivaska A, Niu L. Carbon 2008;46:1687–92.
- [23] Wang J, Chu H, Li Y. ACS Nano 2008;2:2540-6.
- [24] Park HS, Choi BG, Yang SH, Shin WH, Kang JK, Jung D, et al. Small 2009;5: 1754–60.
- [25] Marcilla R, Curri ML, Cozoli PD, Martínez MT, Loinaz I, Grande H, et al. Small 2006;2:507–12.
- [26] Zhang Y, He H, Gao C. Macromolecules 2008;41:9581-94.
- [27] Gao Y, Zhou Y, Yan D. Polymer 2009;50:2572-7.
- [28] Zhang Y, He H, Gao C, Wu J. Langmuir 2009;25:5814–24.
- Huang W, Kim JB, Bruening ML, Baker GL. Macromolecules 2002;35:1175–9.
 Chang Y, Shu SH, Shih YJ, Chu CW, Ruaan RC, Chen WY. Langmuir 2010;26:
- 3522–30.
- [31] He X, Yang W, Pei X. Macromolecules 2008;41:4615-21.
- [32] Ding S, Tang H, Radosz M, Shen Y. J Polym Sci Part A Polym Chem 2004;42: 5794–801.
- [33] Headen TF, Howard CA, Skipper NT, Wilkinson MA, Bowron DT, Soper AK. J Am Chem Soc 2010;132:5735–42.
- [34] Ma JC, Dougherty DA. Chem Rev 1997;97:1303-24.
- [35] Cao Y, Zhang J, Bai Y, Li R, Zakeeruddin SM, Grätzel M, et al. J Phy Chem C 2008;112:13775–81.
- [36] Lee CH, Liu KY, Chang SH, Lin KJ, Lin JJ, Ho KC, et al. J Colloid Interface Sci 2011; 363:635–9.
- [37] Lin PY. Applications of polymerizable ionic liquid and its carbon nanotube composites on electrolytes for dye-sensitized solar cells. National Taiwan University, Master Thesis, 2010.
- [38] Kong H, Gao C, Yan D. J Am Chem Soc 2004;126:412–3.
- [39] Gao C, Vo CD, Jin YZ, Li W, Armes SP. Macromolecules 2005;38:8634–48.
 [40] Fukushima T, Kosaka A, Ishimura Y, Yamamoto T, Takigawa T, Ishii N, et al.
- Science 2003;300:2072–4.
- [41] Okamoto M, Fujigaya T, Nakashima N. Small 2009;5:735-40.
- [42] Sainsbury T, Stolarczyk J, Fitzmaurice D. J Phy Chem B 2005;109:16310-25.