Thiazolium-Containing Poly(ionic liquid)s and Ionic Polymers

*Konrad Grygiel, Laurent Chabanne, Yongjun Men, Jiayin Yuan**

Summary: This paper reports on the synthesis of a new type of ionic polymers, including poly(ionic liquid)s, which contain 4-methylthiazolium-based ionic liquid pending groups along the polymer chain. The monomers were prepared via simple quaternization reaction of 4-methyl thiazole with 4-vinylbenzyl chloride and the subsequentanion exchange with various anions. Free radical polymerization and anion exchange reactions were employed to prepare several 4-methylthiazolium-based ionic polymers. These polymers show anion-dependent tuneable solubility in water and organic solvents. In addition, the new polycations' ability to stabilize single-walled as well as multi-walled carbon nanotubes in water and acetone is presented.

Keywords: ionic liquid; ionic polymers; stabilization; thiazolium ionic liquid

Introduction

One century history of ionic liquids (ILs) has brought abundant types of organic and some inorganic ions for salts which melt below 100 °C.[1] It is believed that the asymmetric chemical structure, low intermolecular interactions as well as weak tendencyto coordinate with oppositely charged ions are the most noticeable factors to lower down the melting point of ionic substance. The reason why ILshavedrawn widespread attention among scientists from various fields are their extraordinary properties, such as superior thermal stability, high ionic conductivity, non-flammability, high heat capacity, negligible vapour pressure, strong polarizability and solubilizing effect.[2–6] This property profile opens a wide applicationspectrum for ILs. Scientists have investigated ILsas solvents in different reactions, catalysts, stabilizers for various particles, and polymer additives.[7–11] Moreover, certain ILs appear to be very good solvents of biopolymers that are usually insoluble in common organic solvents, for instance cellulose.[12]

In order to implement some of the above-mentioned unique properties into solid state materials, researchers are nowadays studying the possible covalent incorporation of ILs into polymers. It allows one to enhance mechanical stability, and improveprocessability, durability and spatial control of ILs.[13–15] These polymers can be conveniently synthesized from a monomeric IL (m.p. below 100 °C) or an organic saltcontaining IL moiety. The most common approach involves free radical polymerization,[16–18] but modern polymerization techniques, such as atom transfer radical polymerization,[19,20] cobalt-mediated radical polymerization,[21] reversible addition-fragmentation transfer polymerization,[22,23] ring opening metathesis polymerization[24] and "click chemistry"[25–27] have been also employed for that purpose. It is worth noting that a high density of ILs in the polymer chains allows one tointroduce IL chemistry into the polymer research. For example, compared to common polyelectrolytes, the IL-rich polymers are usually soluble in organic solvents and show tuneable solubility depending on counter ion.[28,29] Among polycation, polyanion

---

Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Am Mühlenberg 1, OT Golm, D-14476 Potsdam, Germany
E-mail: jiayin.yuan@mpikg.mpg.de

as well as polyzwitterion polymers, polycations are the most popular.[30–40] Typically employed polymerizable cationic species are imidazolium,[16,41–52] tetraalkyl ammonium or phosphonium,[52–54] pyridinium,[55,56] piperidinium,[57] pyrrolidinium,[58] pyrrolium[57] and triazolium.[25,30] Substances bearing thiazolium cations are widely known in the field of ILs. However, thiazoliumcation-based ionic polymers have been rarely reported so far.[5,59] Thiazolium ILs have been reported as precursors of carbenes.[60] Moreover, thiazolium-type ILscan be employed as catalysts for benzoin condensation[61] and Stetter reactions[62,63] as well as for gas separation.[64] They also offer some ionic conductivity and show strong binding to Au.Thiazolium salts have been also used for the preparation of nitrogen – sulphur co-doped carbons showing tuneable degree of doping as well as catalytic monolayers on a gold substrate.[65,66] Considering the interesting features of thiazoliumcations, this paper is devoted to the introduction of 4-methylthiazolium-based IL species into the ionic polymer family. Some of these polymers can be classified as poly(ionic liquid)s or polymerized ionic liquids.

On the other hand, carbon nanotubes (CNTs) show extraordinary mechanical, electrical, chemical, optical and thermal properties. Due to the multitude of possible applications of CNTs in such meaningful areas as drug delivery,[67] nanoelectronics[68] or optical sensors,[69] they have attracted tremendous interest. One of the main drawbacks of CNTs, which has to be overcome, is their tendency to agglomerate due to hydrophobic interactions. It may effectively disenable their functions in some applications. Therefore CNTs in liquids, usually in water, need to be stabilized. It could be achieved by using a deagglomeration agent, which is able to stabilize CNTs after their exfoliation into individual tubes from bundles. Typical approaches applied for this purpose might be divided into two groups – described as "covalent" or "physical" methods. The first one assumes creating covalent bonds between surface of CNTs and the stabilization agent.[70] Unfortunately this method shows a major drawback, because it may disrupt π-networks on CNTs, negatively affecting both mechanical and electronic properties. The second method bases on employing a stabilizing agent, which shows strong non-covalent interactions with CNTs surface.[71,72] The advantage of this approach is that after treatment, CNTs retain their physical properties. It has been reported that several organic compounds or polymers are capable to act as efficient physical stabilizers for CNTs.[73–76] Among them, ability of both ILs as well as PILs to stabilize CNTs has been investigated. Imidazolium-based ILs could support the exfoliation of CNT bundles in the process leading tostable gel-like products.[77,78] The same approach has been employedfor IL monomers in order to synthesize solid composites or polymeric gels. Moreover, CNT dispersions stabilized by PILs could be reversibly transferred from water to organic solvents. It opens the new possibilities of using straightforward methods to processCNTs in order to obtain certain composite materials.[2] As an application example, the newly synthesized thiazolium-based ionic polymers have been tested as dispersant for CNTs in both aqueous solution as well as organic solvents.

Experimental Part

Materials

4-Methylthiazole (99%), potassium hexafluorophosphate (99%) and sodium trifluoromethanesulfonate (98%) were purchased from Alfa Aesar and used without further purification. Lithium bis(trifluoromethylsulfonyl) imide (99%, Io-li-tec), 4-vinylbenzyl chloride (90%, Acros), 2,6-ditertbutyl-4-methyl phenol (99.0%; Aldrich), sodium tetrafluoroborate (98%, Sigma Aldrich), 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (Wake Chemicals),NMR solvents (DMSO-d_6, 99.9%;DMF-d_7, 99.5%; D_2O, 99.9% from Aldrich), single-walled carbon nanotubes (Sigma-Aldrich) and multi-walled carbon nanotubes (Baytubes® C150P) were used as received. All used solvents were of analytic grade.

Monomer Synthesis

4-methyl-3-(4-vinylbenzyl)thiazol-3-ium chloride ($MVBT^+Cl^-$): 4-methylthiazole (20.0 g; 0.20 mol), 2,6-ditertbutylo4-methyl phenol (0.300 g, 1.36 mmol) and ethyl acetate (100 mL) were charged into a 250 mL round bottom flask. Under vigorous stirring 4-chloromethyl styrene (102.6 g; 0.61 mol) was added and stirred at 70 °C for 20 days. Every 5 days, the precipitate was collected by filtration, washed several times with ethyl acetate and dried under high vacuum at 40°C for 24 h (21.45 g, yield 42%).^{1}H NMR (400.1 MHz, D_2O): 7.87 (s, 1H, CH), 7.6 (d, 2H; ArH), 7.3 (d, 2H; ArH), 6.8 (q,1H; CH), 5.9 (d, 1H; CH_2), 5.64 (s, 2H; CH_2), 5.4 (d, 1H; CH_2), 2.50 (s, 3H; CH_3); due to a fast proton exchange of the acidic proton bonded to thiazole ring in D_2O, the peak is absent, however the existence of thisproton was proved in DMSO-$d_6$in Figure 3.

4-methyl-3-(4-vinylbenzyl)thiazol-3-ium bis (trifluoromethylsulfonyl) imide ($MVBT^+TF_2N^-$): $MVBT^+Cl^-$ (1.50 g, 5.96 mmol) was dissolved in 10 mL of water. $LiTF_2N$ (1.82 g, 6.34 mmol) was dissolved in 40 mL of water and added dropwise under vigorous stirring.Phase separation was observed. After 24 h the upper phase was removed. The bottom part was washed with water 3 times, dissolved in 50 mL of methanol, and re-precipitated out in water. The product was collected and dried under high vacuumat 40 °C for 48 h (2.10 g, yield 71%). ^{1}H NMR (400 MHz, DMSO-d_6): 10.14 (s, 1H, CH), 8.05 (s, 1H, CH), 7.5 (d, 2H; ArH), 7.3 (d, 2H; ArH), 6.8 (q,1H; CH), 5.9 (d, 1H; CH_2), 5.7 (s, 2H; CH_2), 5.3 (d, 1H; CH_2), 2.4 (s, 3H; CH_3)

4-methyl-3-(4-vinylbenzyl)thiazol-3-ium hexafluorophosphate ($MVBT^+PF_6^-$): it was obtained in the similar manner to $MVBT^+TF_2N^-$ except that acetone was used instead of methanol for to dissolvethe crude product. (2.15 g, yield 76%).^{1}H NMR (400 MHz, DMSO-d_6): 10.14 (s, 1H, CH), 8.05 (s, 1H, CH), 7.6 (d, 2H; ArH), 7.3 (d, 2H; ArH), 6.8 (q,1H; CH), 5.9 (d, 1H; CH_2),), 5.7 (s, 2H; CH_2), 5.3 (d, 1H; CH_2), 2.4 (s, 3H; CH_3).

4-methyl-3-(4-vinylbenzyl)thiazol-3-ium trifluoromethanesulfonate ($MVBT^+TFO^-$): $MVBT^+Cl^-$(1.50 g, 5.96 mmol), sodium trifluoromethanesulfonate (NaTFO; 1.15 g, 6.55 mmol) and 100 mL of acetonitrile were charged into a round bottom flask and stirred at room temperature for 72 h. Then, the solid particles were centrifuged out. The supernatant was collected, followed by the removal of acetonitrile under reduced pressure. The product was dried under high vacuum at 40 °C for 48 h. ^{1}H NMR (400 MHz, DMSO-d_6): 10.14 (s, 1H, CH), 8.05 (s, 1H, CH), 7.6 (d, 2H; ArH), 7.3 (d, 2H; ArH), 6.8 (q, 1H; CH), 5.9 (d, 1H; CH_2),), 5.74 (s, 2H; CH_2), 5.3 (d, 1H; CH_2), 2.44 (s, 3H; CH_3).

Polymer Synthesis

Two methods were used in this manuscript to prepare ionic polymers, either by direct solution polymerization of $MVBT^+Cl^-$ or by anion exchange with chloride-containing ionic polymerP ($MVBT^+Cl^-$).

P($MVBT^+Cl^-$): $MVBT^+Cl^-$(7.6 g, 30.1 mmol), 2,2′-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (0.23 g, 0.79 mmol) and 40 mL of MiliQ water were loaded into a 100 mL Schlenk flask and stirred. The mixture was degassed by 3 cycles of freeze-pump-thaw procedure. The reaction was carried out under argon at 90 °C for 24 h. The crude product was purified by dialysis against deionized water, and freeze-dried. (6.35 g, yield 84%).

P($MVBT^+TF_2N^-$): P($MVBT^+Cl^-$) (1.00 g, 3.97 mmol of repeating units) was charged into a 100 mL round bottom flask and dissolved in 30 mL of water. $ALiTF_2N$ (1.25 g, 4.35 mmol) solution in 20 mL of MiliQ water was added dropwise under vigorous stirring at room temperature. A white precipitate was observed. After 24 h, the precipitate was filtered off on a Büchner funnel, washed several times with water and dried at 40 °C for 48 h (1.63 g, yield 89%).

P($MVBT^+PF_6^-$): it was obtained in the similar fashion to P($MVBT^+TF_2N^-$), but potassium hexafluorophosphate(0.81 g, 4.36 mmol) was used as exchanged salt. Crude product was purified by centrifugation and 5 times of washing with water (1.03 g, yield 72%).

P(MVBT$^+$TFO$^-$): P(MVBT$^+$Cl$^-$) (100 mg, 0.40 mmol of repeating units), NaTFO (77.0 mg, 0.448 mmol) and 20.0 mL of acetonitrile were charged into a 25 mL round bottom and stirred at room temperature for 24 h. Then, solid particles were centrifuged out. Supernatant was collected followed by removal of acetonitrile under reduced pressure. Crude product was washed with water, dried under high vacuum at 40 °C for 48 h (109.1 mg, yield 75%).

Stabilization of CNTs

In the case of stabilization of MWCNTs and SWCNTs, 1.0 mg of CNTs, 100 mg of P(MVBT$^+$Cl$^-$) and 25 mL of water were charged into a beaker. The mixture was then sonicated using a Branson Digital Sonifier model W450D (60% of amplitude, 10 min, 5 s on/15 s off). During the sonication the beaker was placed in an ice bath. A black dispersion formed that was stable for weeks. For anion exchange, 15 mL of the stable MWCNTs/P(MVBT$^+$Cl$^-$) dispersion was transferred to a 25 mL vial and KPF_6 (80 mg, 0.43 mmol) solution in 10 mL of water was added dropwise. After 24 hours, the black precipitate was centrifuged out, washed 5 times with water, and re-dispersed in acetone.

Characterization

Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded at room temperature using a Bruker DPX-400 spectrometer operating at 400.1 MHz.The carbon nuclear magnetic resonance (^{13}C-NMR) and the heteronuclear multiple bond correlation (^{1}H-^{13}C HMBC) NMR spectra were recorded at room temperature on a VARIAN 400-MR (400 MHz) spectrometer. DMSO-d_6 was used as a solvent for all measurements except MVBT$^+$Cl$^-$, for which D_2O was also used to avoid peaks overlap.

Differential scanning calorimetry (DSC) measurements were done under a nitrogen flow at a heating rate of 10 K min^{-1} using a Perkin-Elmer DSC-1 instrument.

Thermogravimetric analysis (TGA) experiments were performed under a nitrogen flow at a heating rate of 10 K min^{-1} using a Netzsch TG209-F1 apparatus.

Elemental analysis was accomplished as a combustion analysis using a Vario Micro device.

Gel permeation chromatography (GPC) was performed using NOVEMA-column with mixture of 80% of acetatebuffer and 20% of methanol (flow rate 1.00 mL min^{-1}, PEO standards using RI detector - Optilab-DSP-InterferometricRefractometer (Wyatt-Technology).

Transmission electron microscopy (TEM) measurementswere performed on a Zeiss EM 912 Omega microscope operating at 120 kV. TEM samples were prepared by dropping 5 μL of a diluted stabilized CNT dispersion on a 200 mesh carbon-coated copper TEM grid.

Solubility tests were performed by mixing 10 mg of ionic polymer samples with different solvents (1 weight percent) in 5 mL vials. After 24 h of shaking, the presence of solid inside the vials was checked.

Results

The synthetic route to monomers and ionic polymers is shown in Figure 1. The monomer with chloride as anion was synthesized via the quaternization reaction of 4-methyl thiazole and 4-vinylbenzyl chloride in ethyl acetate at 70 °C in the presence of 2,6-ditertbutylo 4-methyl phenol as an inhibitor to avoid the polymerization of the styrenic unit. This reaction leads to the formation of a thiazolium monomer 4-methyl-3-(4-vinylbenzyl)thiazol-3-ium chloride (MVBT$^+$Cl$^-$). The polymer P-(MVBT$^+$Cl$^-$) was prepared directly via free radical polymerization of MVBT$^+$Cl$^-$ at 90 °C in water for 24 h using a non-ionic thermal initiator 2,2′-azobis[2-methyl-N-(2-hydroxyethyl) propionamide] (VA86). Anion exchange reactions are frequently used in IL chemistry to modify the physical/

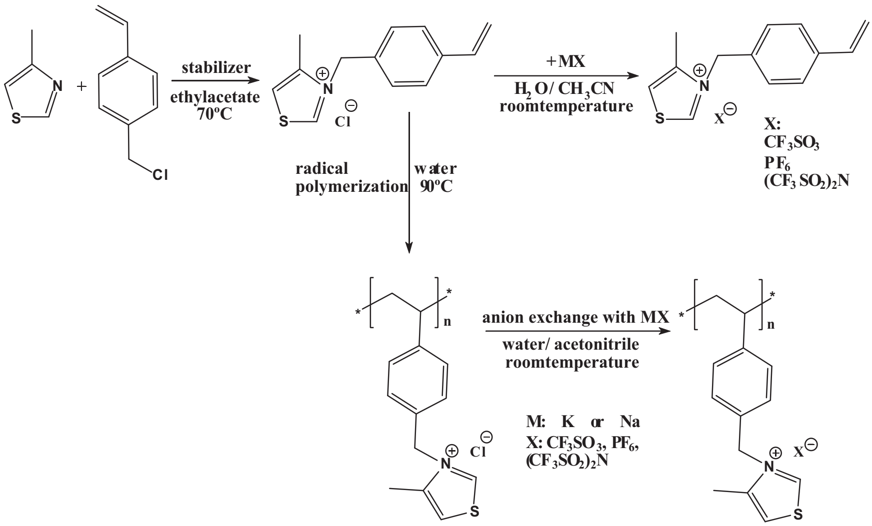

Figure 1.
Synthetic route and chemical structures of the obtained thiazolium-type ILmonomersand ionic polymers.

chemical properties of the ILs. Here, anion exchange was performed to both $MVBT^+Cl^-$ and $P(MVBT^+Cl^-)$ to replace the chloride with hexafluorophosphate, triflurosulfonate and bis(trifluoromethanesulfonate)imide anions. It should be mentioned that direct solution polymerization of non-halide thiazolium IL monomers in DMF has been tried in this study as well. However, as opposed to the polymerization of monomer $MVBT^+Cl^-$, these runs failed to provide the non-halide ionic polymers. These polymers were then prepared via the anion exchange with $P(MVBT^+Cl^-)$.

The chemical structure of monomer $MVBT^+Cl^-$ was confirmed by proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) and carbon nuclear magnetic resonance spectroscopy(^{13}C-NMR). In the thiazole monomers, both the nitrogen and the sulphur can potentially undergo quaternization. In order to assess whether the product was indeed obtained by creating a bond between 4-vinylbenzyl groups and the nitrogen instead of the sulphur atom of the thiazole ring, a proton-carbon heteronuclear multiple bond correlation (^{1}H-^{13}CHMBC) measurement was performed. The spectrum data agreed well with the proposed structure. In Figure 2, the HMBC correlation is shown. As can be clearly seen, the spectrum showedthe direct coupling between proton 10 and carbon 2, but no coupling between proton 10 and carbon 8 was observed. It allows us also to detect that carbon 10 is coupled to proton 1, but not to proton 8. The ^{1}H/^{13}C couplings thus indicate that the obtained pure product was synthesized via bonding of 4-vinylbenzyl group to the nitrogen atom, i.e. the quaternization reaction took place only onthe nitrogen rather than the sulphur in the thiazole ring.

The anion exchange reactions with $MVBT^+Cl^-$ and $P(MVBT^+Cl^-)$ were performed using two different methods. In the case of TF_2N^- and $PF_6{}^-$ counter anions, the anion exchange proceeded by dropping an aqueous solution of the corresponding salt into the monomer or polymer solution. Following the addition of the salt solution, flocculation occurred immediately. This is indicative of the replacement of the hydrophilic chloride anion by the hydrophobic $PF_6{}^-$ or Tf_2N^- anions, which turn the monomer $MVBT^+Cl^-$ orpolymer $P(MVBT^+Cl^-)$ insoluble in aqueous solution. In the case of TFO^- anion, the anion exchange with chloride proceeded by simply mixing 1.1 mol equivalent of NaTFO

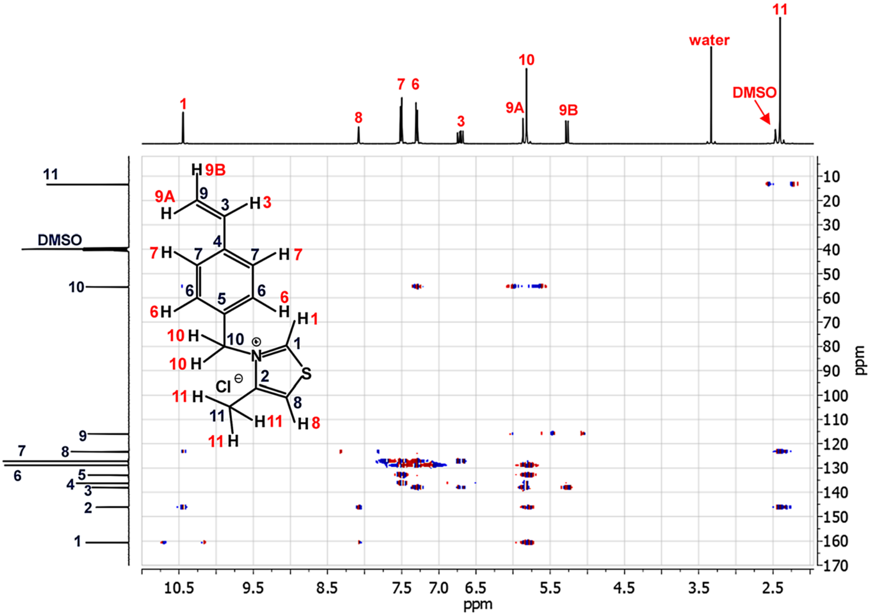

Figure 2.
^{1}H-^{13}C HMBC spectrum of monomer MVBT^{+}Cl^{-}.

with MVBT^{+}Cl^{-} or P(MVBT^{+}Cl^{-}) in dry acetonitrile. Following the slow dissolution of these two salts, NaCl precipitated out of the solution due to its rather low solubility in acetonitrile. After filtration to remove NaCl, the monomers with TFO^{-} anions were obtained by evaporating acetonitrile under high vacuum at room temperature.

Figure 3 shows the ^{1}H-NMR spectraof MVBT^{+}Cl^{-}, MVBT^{+}TF$_2$N^{-} and their corresponding polymers in DMSO-d_6. In case of MVBT^{+}TF$_2$N^{-} synthesized from MVBT^{+}Cl^{-}, it shows very similar spectrum pattern. Only a noticeable shift of the two thiazoliumcation ring was observed, for instance, from 10.59 (proton 1) and 8.14 ppm (proton 8) to 10.14 and 8.05 ppm, respectively. We observed analogous peak shifts in theproducts of other monomers with PF$_6$$^{-}$ and TFO^{-} anions. The melting points of these monomer samples were determined by DSC. MVBT^{+}TF$_2$N^{-} and MVBT^{+}TFO^{-} showed melting points at 60 and 69 °C, respectively (Figure 4). According to the definition, they are classified as classic ionic liquids and their corresponding polymers are poly(ionic liquid)s. For other obtained monomers no melting endotherms were observed in the DSC traces up to 100 °C, thus they belong to organic salts, and therefore their corresponding polymers are in the general scope of ionic polymers.

Figure 3C shows the ^{1}H-NMR spectrum of P(MVBT^{+}Cl^{-}). Compared with its monomer spectrum in Figure 3A, we can

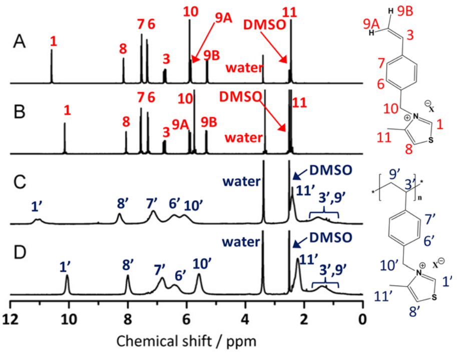

Figure 3.
^{1}H-NMR spectra of: A) monomer MVBT^{+}Cl^{-}; B) monomer MVBT^{+}TF$_2$N^{-}; C) polymer P(MVBT^{+}Cl^{-}); D) polymer P(MVBT^{+}TF$_2$N^{-}).

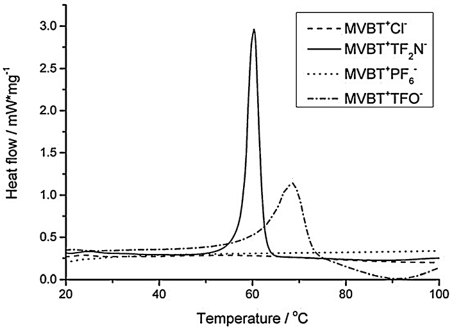

Figure 4.
DSC curves recorded for ionic monomers.

observe broadening of some particular peaks as well as the disappearance of the vinyl group signals at 6.73, 5.84, and 5.29 ppm after the reaction. Moreover, the appearance of a broad signal in thehigh field range (between 1 and 2 ppm), which can be attributed to protons connected to polymer backbone, is clearly seen. Figure 3D shows the ^{1}H-NMR spectrum of P(MVBT$^+$TF$_2$N$^-$) prepared via anion exchange reaction from P(MVBT$^+$Cl$^-$). After the reaction, both resonance signals of protons of the thiazolium ring at 11.0, 8.3 ppm as well as a peak of the CH$_2$ group at 6.1 ppm shift to 10.1, 8.0 and 5.6 ppm, respectively. The ^{1}H-NMR spectra of the other anion-exchanged polymers resemble that of P(MVBT$^+$TF$_2$N$^-$).

The molecular weight of these polymers was determined by gel permeation chromatography. Figure 5 shows the elugram of P(MVBT$^+$Cl$^-$).It displayed a monomodal distribution of P(MVBT$^+$Cl$^-$). The number-average molecular weight of the polymer (measured in water, calculated using PEO standard) was 15,000 g/mol with a polydispersity index of 3.0, which is expected from a free radical polymerization. Since the other non-halide ionic polymers were prepared via anion exchange with P(MVBT$^+$Cl$^-$), the degree of polymerization and the molecular weight distribution are similar to P(MVBT$^+$Cl$^-$).

Thermal behavior of the obtained thiazolium polymers was evaluated by TGA. As expected, polymerization of monomer MVBT$^+$Cl$^-$ results in the elevation of the decomposition temperature (defined as 10 wt%) from 170 °C for MVBT$^+$Cl$^-$ to 200 °C in the case of P(MVBT$^+$Cl$^-$) (Figure 6). The initial weight loss in the MVBT$^+$Cl$^-$ monomer from 100–150 °C is due to the evaporation of trace amount of water due to a limited drying temperature, which is necessarily low to avoid thermal polymerizations.According to previous study, thermal stability of ionic liquid-containing polymers can be tuned by anion exchange reactions.[82] Altering anions from chloride to less basic, fluorinated anions allows to further elevate T$_d$ of polymers, for instance even 280 °C in the case of PMVBT$^+$TF$_2$N$^-$. Thermal stability of P(MVBT$^+$PF$_6^-$) and P(MVBT$^+$TFO$^-$) was enhanced as well when compared to

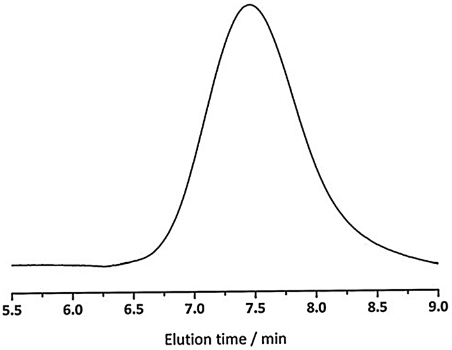

Figure 5.
GPC trace measured for P(MVBT$^+$Cl$^-$).

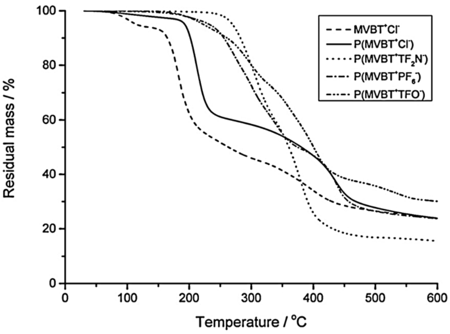

Figure 6.
TGA curves of the IL monomer MVBT$^+$Cl$^-$ and the synthesized ionic polymers under nitrogen atmosphere.

$P(MVBT^+Cl^-)$. So the thermal stability of the thiazolium-based ionic polymers follows the sequence of $Cl^- < PF_6^-$, $TFO^- < Tf_2N^-$. The obtained data indicate a strong correlation between the type of counteranion and the thermal properties of the synthesized ionic polymers. As expected, introducing bigger anions, whosecharge is more effectively delocalized to decrease the chain-chain interaction, can significantly lower down the T_g of polymers.[82,83]

Another effect of the anion exchange is the solubility property of the polymers.The results of the solubility tests are summarized in Table 1. $P(MVBT^+Cl^-)$ bearing hydrophilic Cl^- counteranion was soluble in water as well as in polar organic solvents of high polarity (e.g. in methanol). Hydrophobic solvents as well as organic solvents with medium polarity (THF, chloroform and acetone) cannot dissolve this polymer. Unexpectedly, this polymer was found to be insoluble in DMF despite of several tries. Exchanging counteranions to more hydrophobic ones enables them to be soluble in DMF. Moreover the polymers with PF_6^- and TF_2N^- anionsbecame soluble in acetone, whilethose bearingPF_6^- were not soluble in methanol anymore. It should be mentioned that all obtained polymer products show fairly good solubility in dimethyl sulfoxide.

The capability of these thiazolium-based ionic polymers to stabilize multi walled carbon nanotubes (MWCNTs) as well as single walled carbon nanotubes (SWCNTs) in water was also discussed. Stabilization was performed in asimilar manner to the literature procedure employed for poly(ionic liquid)s bearing imidazoliumcations.[84] By sonication of MWCNTs and $P(MVBT^+Cl^-)$ in aqueous media a homogenous, dark and stable dispersion was obtained (Figure 7A and 7B). As depicted in Figure 7C and 7D, very good quality of the CNT dispersion was confirmed using transmission electron microscopy (TEM). The observed MWCNTs were well separated, without the presence of large

Table 1.
Solubility tests of $P(MVBT^+X^-)$in different solvents.

$P(MVBT^+X)$	H_2O	MeOH	acetone	DMF	DMSO	THF, EtAc, toluene, $CHCl_3$
Cl^-	+	+	–	–	+	–
TFO^-	–	+	–	+	+	–
PF_6^-	–	–	+	+	+	–
Tf_2N^-	–	+	+	+	+	–

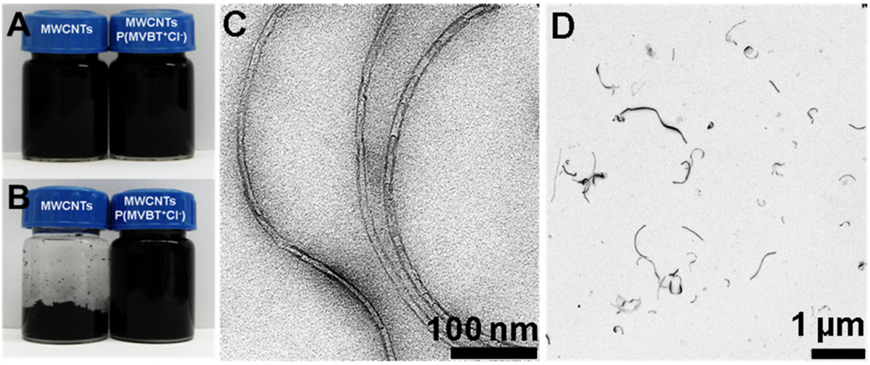

Figure 7.
A) Photographs of MWCTs dispersionin waterand $P(MVBT^+Cl^-)$ stabilized MWCNs dispersionin waterimmediately after sonication; B) Photographs of MWCT dispersionin waterand $P(MVBT^+Cl^-)$ stabilized MWCN dispersionin water24 h after sonication; C and D) TEM images of $P(MVBT^+Cl^-)$ stabilized MWCNT dispersion.

agglomerates. A control experiment was also performed, where MWCNTs were dispersed in water using ultrasonic horn, but precipitation was observed shortly after the sonication. The same results were obtained for SWCNTs as well. It is widely known, that imidazolium cation can support the stabilization of CNT dispersions via the cation-π interaction.[85,86] According to our results, thiazoliumcations in ionic polymer offer similar solubilizing effect. Moreover, MWCNTs stabilized with the thiazolium polymer can be easily transferred to organic solvents, such as acetone. This was performed by precipitating P($MVBT^+Cl^-$)-stabilized MWCNTs from their aqueous dispersion by adding KPF_6 solution. This leads to theanion exchange between Cl^- and PF_6^-on the polymer and turns the MWCNT surface hydrophobic. The precipitated MWCNTs become then soluble in acetone.

Conclusion

In summary, a series of thiazolium-based monomers and ionic polymers have been studied in detail. The $MVBT^+Cl^-$ monomer was first prepared by simple quaternization of 4-methyl thiazole with 4-vinylbenzyl chloride. The quaternization reaction occurred selectively at the nitrogen atom rather than the sulfur atom in the thiazolemolecule, as confirmed using ^1H-^{13}CHMBC NMR spectroscopy. The ionic polymer P($MVBT^+Cl^-$) was obtained via free radical polymerization of $MVBT^+Cl^-$. Thiazolium-based monomers bearing fluorinated anions were prepared by anion exchange to afford non-halide monomers. Their polymers were obtained via anion exchange reaction of the P($MVBT^+Cl^-$)polymer. The Tf_2N^- and TFO^--based monomers and polymers can be classified as classic ILs and poly(ionic liquid)s. These new ionic polymers were fully characterized and exhibited excellent ability to stabilize CNTs in water and organic solvents.

Acknowledgements: We acknowledge financial support from the Max Planck Society and the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007–2013 under REA grant agreement no 289347. This work was also partially supported by the European COST programme, Action No MP1202, section Materials, Physics and Nanosciences.

[1] J. S. Wilkes, *Green Chem.* **2002**, *4*, 73.

[2] J. Yuan, M. Antonietti, *Polymer* **2011**, 52, 1469.

[3] N. V. Tsarevsky, K. Matyjaszewski, *Chem. Rev.* **2007**, *107*, 2270.

[4] M. Isik, R. Gracia, L. C. Kollnus, L. C. Tomé, I. M. Marrucho, D. Mecerreyes, *ACS Macro Lett.* **2013**, 975.

[5] Y. Yoshida, O. Baba, G. Saito, *J. Phys. Chem. B* **2007**, *111*, 4742.

[6] M. Yoshio, T. Mukai, H. Ohno, T. Kato, *J. Am. Chem. Soc.* **2004**, *126*, 994.

[7] F. Liu, L. Wang, Q. Sun, L. Zhu, X. Meng, F.-S. Xiao, *J. Am. Chem. Soc.* **2012**, *134*, 16948.

[8] J. Pinaud, J. Vignolle, Y. Gnanou, D. Taton, *Macromolecules* **2011**, 44, 1900.

[9] Y. Kohno, H. Ohno, *Chem. Commun.* **2012**, *48*, 7119.

[10] Z. Chen, F. Yan, L. Qiu, J. Lu, Y. Zhou, J. Chen, Y. Tang, J. Texter, *Langmuir* **2010**, *26*, 3803.

[11] Y. Zhou, L. Qiu, Z. Deng, J. Texter, F. Yan, *Macromolecules* **2011**, 44, 7948.

[12] R. P. Swatloski, S. K. Spear, J. D. Holbrey, R. D. Rogers, *J. Am. Chem. Soc.* **2002**, *124*, 4974.

[13] O. Green, S. Grubjesic, S. Lee, M. A. Firestone, *Polym. Rev. (Philadelphia, PA, U.S.)* **2009**, *49*, 339.

[14] Q. Zhao, T.-P. Fellinger, M. Antonietti, J. Yuan, *Macromol. Rapid Commun.* **2012**, *33*, 1149.

[15] Q. Zhao, P. Zhang, M. Antonietti, J. Yuan, *J. Am. Chem. Soc.* **2012**, *134*, 11852.

[16] M. Hirao, K. Ito, H. Ohno, *Electrochimica Acta* **2000**, 45, 1291.

[17] D. Batra, S. Seifert, L. M. Varela, A. C. Y. Liu, M. A. Firestone, *Adv. Funct. Mater.* **2007**, *17*, 1279.

[18] J. Yuan, S. Wunder, F. Warmuth, Y. Lu, *Polymer* **2012**, 53, 43.

[19] X. He, W. Yang, X. Pei, *Macromolecules* **2008**, *41*, 4615.

[20] J. Texter, V. A. Vasantha, R. Crombez, R. Maniglia, L. Slater, T. Mourey, *Macromol. Rapid Commun.* **2012**, *33*, 69.

[21] C. Detrembleur, A. Debuigne, M. Hurtgen, C. Jérôme, J. Pinaud, M. v. Fèvre, P. Coupillaud, J. Vignolle, D. Taton, *Macromolecules* **2011**, 44, 6397.

[22] K. Vijayakrishna, S. K. Jewrajka, A. Ruiz, R. Marcilla, J. A. Pomposo, D. Mecerreyes, D. Taton, Y. Gnanou, *Macromolecules* **2008**, *41*, 6299.

[23] J. Yuan, H. Schlaad, C. Giordano, M. Antonietti, *Eur. Polym. J.* **2011**, *47*, 772.

[24] Y. S. Vygodskii, A. S. Shaplov, E. I. Lozinskaya, K. A. Lyssenko, D. G. Golovanov, I. A. Malyshkina, N. D. Gavrilova, M. R. Buchmeiser, *Macromol. Chem. Phys.* **2008**, *209*, 40.

[25] P. Dimitrov-Raytchev, S. Beghdadi, A. Serghei, E. Drockenmuller, *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 34.

[26] J. Yuan, D. Mecerreyes, M. Antonietti, *Prog. Polym. Sci.* **2013**, *38*, 1009.

[27] A. S. Shaplov, P. S. Vlasov, E. I. Lozinskaya, O. A. Shishkan, D. O. Ponkratov, I. A. Malyshkina, F. Vidal, C. Wandrey, I. A. Godovikov, Y. S. Vygodskii, *Macromol. Chem. Phys.* **2012**, *213*, 1359.

[28] R. Marcilla, J. Alberto Blazquez, J. Rodriguez, J. A. Pomposo, D. Mecerreyes, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 208.

[29] O. Mel'nik, A. Shaplov, E. Lozinskaya, N. Popova, M. Makarov, I. Odinets, K. Lysenko, G. Timofeeva, I. Malyshkina, Y. Vygodskii, *Polym. Sci. Ser. B* **2010**, *52*, 316.

[30] D. Mecerreyes, *Prog. Polym. Sci.* **2011**, *36*, 1629.

[31] S. Cheng, M. Zhang, T. Wu, S. T. Hemp, B. D. Mather, R. B. Moore, T. E. Long, *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 166.

[32] W. Ogihara, S. Washiro, H. Nakajima, H. Ohno, *Electrochimica Acta* **2006**, *51*, 2614.

[33] M. D. Green, T. E. Long, *Polym Rev* **2009**, *49*, 291.

[34] J. Texter, *Macromol. Rapid Commun.* **2012**, *33*, 1996.

[35] H. Ohno, *Macromol. Symp.* **2007**, *249–250*, 551.

[36] A. S. Shaplov, P. S. Vlasov, M. Armand, E. I. Lozinskaya, D. O. Ponkratov, I. A. Malyshkina, F. Vidal, O. V. Okatova, G. M. Pavlov, C. Wandrey, I. A. Godovikov, Y. S. Vygodskii, *Polymer Chemistry* **2011**, *2*, 2609.

[37] M. Koebe, M. Drechsler, J. Weber, J. Yuan, *Macromol. Rapid Commun.* **2012**, *33*, 646–651.

[38] Y. Men, X.-H. Li, M. Antonietti, J. Yuan, *Polym. Chem.* **2012**, *3*, 871.

[39] Q. Zhao, M. Yin, A. P. Zhang, S. Prescher, M. Antonietti, J. Yuan, *J. Am. Chem. Soc.* **2013**, *135*, 5549.

[40] P. Zhang, J. Yuan, T.-P. Fellinger, M. Antonietti, H. Li, Y. Wang, *Angew. Chem., Int. Ed.* **2013**, *52*, 6028.

[41] M. D. Green, D. Wang, S. T. Hemp, J.-H. Choi, K. I. Winey, J. R. Heflin, T. E. Long, *Polymer* **2012**, *53*, 3677.

[42] J. Yuan, S. Soll, M. Drechsler, A. H. E. Müller, M. Antonietti, *J. Am. Chem. Soc.* **2011**, *133*, 17556.

[43] R. Marcilla, E. Ochoteco, C. Pozo-Gonzalo, H. Grande, J. A. Pomposo, D. Mecerreyes, *Macromol. Rapid Commun.* **2005**, *26*, 1122.

[44] Y. Ye, Y. A. Elabd, *Macromolecules* **2011**, *44*, 8494.

[45] R. L. Weber, Y. Ye, A. L. Schmitt, S. M. Banik, Y. A. Elabd, M. K. Mahanthappa, *Macromolecules* **2011**, *44*, 5727.

[46] D. England, N. Tambe, J. Texter, *ACS Macro Lett.* **2012**, *1*, 310.

[47] Q. Zhao, S. Soll, M. Antonietti, J. Yuan, *Polymer Chemistry* **2013**, *4*, 2432.

[48] A. Wilke, J. Yuan, M. Antonietti, J. Weber, *ACS Macro Lett.* **2012**, 1028.

[49] L. Zhao, R. Crombez, F. P. Caballero, M. Antonietti, J. Texter, M.-M. Titirici, *Polymer* **2010**, *51*, 4540.

[50] F. Yan, J. Texter, *Adv. Colloid Interface Sci.* **2006**, *128–130*, 27.

[51] K. Tauer, N. Weber, J. Texter, *Chem. Commun.* **2009**, 6065.

[52] Y. Men, H. Schlaad, J. Yuan, *ACS Macro Lett.* **2013**, *2*, 456.

[53] S. Supasitmongkol, P. Styring, *Energy Environ. Sci.* **2010**, *3*, 1961.

[54] P. G. Mineo, L. Livoti, M. Giannetto, A. Gulino, S. Lo Schiavo, P. Cardiano, *J. Mater. Chem.* **2009**, *19*, 8861.

[55] M. Watanabe, S-i. Yamada, N. Ogata, *Electrochim. Acta* **1995**, *40*, 2285.

[56] J. Yuan, A. G. Marquez, J. Reinacher, C. Giordano, J. Janek, M. Antonietti, *Polym. Chem.* **2011**, *2*, 1654.

[57] W. S. Ogihara, H. Nakajima, H. Ohno, *Electrochimica Acta* **2006**, *51*, 6.

[58] A.-L. Pont, R. Marcilla, I. De Meatza, H. Grande, D. Mecerreyes, *J. Power Sources* **2009**, *188*, 558.

[59] J. H. Davis, Jr, K. J. Forrester, *Tetrahedron Lett.* **1999**, *40*, 1621.

[60] A. J. Arduengo, J. R. Goerlich, W. J. Marshall, *Liebigs Annalen* **1997**, *1997*, 365.

[61] J. Castelk, F. Lopez-Calahorra, L. Domingo, *J. Org. Chem.* **1988**, *53*, 4.

[62] A. G. M. Barrett, A. C. Love, L. Tedeschi, *Org. Lett.* **2004**, *6*, 3377.

[63] Z.-Z. Zhou, F.-Q. Ji, M. Cao, G.-F. Yang, *Adv. Synth. Catal.* **2006**, *348*, 1826.

[64] P. C. Hillesheim, S. M. Mahurin, P. F. Fulvio, J. S. Yeary, Y. Oyola, D-e. Jiang, S. Dai, *Ind. Eng. Chem. Res.* **2012**, *51*, 11530.

[65] J. P. Paraknowitsch, B. Wienert, Y. Zhang, A. Thomas, *Chem.-Eur. J.* **2012**, *18*, 15416.

[66] K. Moteshareі, D. C. Myles, *J. Am. Chem. Soc.* **1997**, *119*, 6674.

[67] A. Bianco, K. Kostarelos, M. Prato, *Curr. Opin. Chem. Biol.* **2005**, *9*, 674.

[68] Q. Cao, J. A. Rogers, *Adv. Mater.* **2009**, *21*, 29.

[69] P. W. Barone, S. Baik, D. A. Heller, M. S. Strano, *Nat. Mater.* **2005**, *4*, 86.

[70] S. Qin, D. Qin, W. T. Ford, D. E. Resasco, J. E. Herrera, *J. Am. Chem. Soc.* **2003**, *126*, 170.

[71] W. Peng, C. Xing, H. Nancy, T. Un Chong, B. Ola, Z. Alex, *R. B. Carolyn. Angew. Chem.* **2008**, *120*, 5100.

[72] V. C. Tung, J. Kim, L. J. Cote, J. Huang, *J. Am. Chem. Soc.* **2011**, *133*, 9262.

[73] S. Meuer, L. Braun, R. Zentel, *Macromol. Chem. Phys.* **2009**, *210*, 1528.

[74] M. Zheng, A. Jagota, E. D. Semke, B. A. Diner, R. S. McLean, S. R. Lustig, R. E. Richardson, N. G. Tassi, *Nat. Mater.* **2003**, *2*, 338.

[75] D. Wang, W.-X. Ji, Z.-C. Li, L. Chen, *J. Am. Chem. Soc.* **2006**, *128*, 6556.

[76] M. Antonietti, Y. Shen, T. Nakanishi, M. Manuelian, R. Campbell, L. Gwee, Y. A. Elabd, N. Tambe, R. Crombez, J. Texter, *ACS Appl. Mater. Interfaces* **2010**, *2*, 649.

[77] T. Fukushima, T. Aida, *Chem.-Eur. J.* **2007**, *13*, 5048.

[78] T. Fukushima, A. Kosaka, Y. Ishimura, T. Yamamoto, T. Takigawa, N. Ishii, T. Aida, *Science* **2003**, *300*, 2072.

[79] J. P. Paraknowitsch, A. Thomas, *Energy Environ. Sci.* **2013**, *6*, 2839.

[80] J. P. Paraknowitsch, A. Thomas, J. Schmidt, *Chem. Commun. (Cambridge, U. K.)* **2011**, *47*, 8283.

[81] S.-A. Wohlgemuth, R. J. White, M.-G. Willinger, M.-M. Titirici, M. Antonietti, *Green Chem.* **2012**, *14*, 1515.

[82] C. P. Fredlake, J. M. Crosthwaite, D. G. Hert, S. N. V. K. Aki, J. F. Brennecke, *J. Chem. Eng. Data* **2004**, *49*, 954.

[83] R. S. Bhavsar, S. C. Kumbharkar, U. K. Kharul, *J. Membr. Sci.* **2012**, *389*, 305.

[84] S. Soll, M. Antonietti, J. Yuan, *ACS Macro Lett.* **2011**, *1*, 84.

[85] R. Marcilla, M. L. Curri, P. D. Cozzoli, M. T. Martínez, I. Loinaz, H. Grande, J. A. Pomposo, D. Mecerreyes, *Small* **2006**, *2*, 507.

[86] S. Bellayer, J. W. Gilman, N. Eidelman, S. Bourbigot, X. Flambard, D. M. Fox, H. C. De Long, P. C. Trulove, *Adv. Funct. Mater.* **2005**, *15*, 910.