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Imidazolium end-functionalized ATRP polymers as directing agents for carbon nanotube dispersion and confinement^a

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Imidazolium end-functionalized poly(n-butyl acrylate) and poly(styrene) (co)polymers were synthesized via atom transfer radical polymerization. The polymers were tested as dispersing/compatibilizing agents of carbon nanotubes (CNTs) in polymer matrices. By selecting the proper ω -imidazolium polymer, it was possible to direct the CNT confinement towards a specific polymer phase within polymer mixtures.

Introduction

Since their first observation by Iijima in the beginning of the nineties, carbon nanotubes (CNTs) have attracted a lot of attention due to their exceptional properties.^[1] Besides their nanometric size, their mechanical, thermal, structural and electrical performances allow for

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^a **Supporting Information** is available at Wiley Online Library or from the author. ((Other reference to the authors can also appear here, such as Author-One and Author-Two contributed equally to this work.))

their use in a wide variety of applications like electronic components, chemical and biological sensors, electron field emitters, and energy storage components. ^[2] A key parameter for producing nanocomposite materials with largely improved physical properties relies on the extent of dispersion of the individual CNTs. However, the CNTs tend to aggregate as a result of numerous van der Waals (π - π) interactions between the tubes, and by entanglements, which occur during their synthesis. As a result, the homogeneous dispersion of CNTs in polymer matrices is relatively difficult to achieve. Only by improving the affinity between the CNT surface and the polymer matrix, individualization of the nanotubes is made possible. Various strategies have been developed in order to achieve such improvements, based on either covalent or non-covalent functionalization of the CNT surface with polymer chains. ^[3] However, in case of covalent functionalization, structural defects are usually formed on the CNT surface, deteriorating the intrinsic properties of the nanotubes and consequently of the nanocomposites. In this regard, non-covalent functionalization is a preferred method for stabilization of CNTs as the electronic structure and the original CNT properties are preserved. Various supramolecular interactions can be envisioned, such as π - π stacking, cation- π interactions, amine-aromatic charge transfer, and dipole/dipole electrostatic interactions. Recently, the imidazolium function has been investigated as one of the strongest supramolecular anchoring moiety for CNTs. ^[4] In this respect, L-lactide was polymerized via ring opening polymerization starting from a hydroxy-containing imidazolium initiator. The imidazolium-functionalized PLLA was used as an efficient stabilizer for CNTs both in solution and in PLLA matrix. The aim of this work is to extend this strategy to polymers such as poly(styrene) (PSty) and poly(n-butyl acrylate) (PnBuA). Both polymers were selected for their difference in thermal properties on basis of their glass transition temperature (T_g). Indeed, PSty is a glassy ($T_g \sim 100^\circ\text{C}$) thermoplastic polymer with applications ranging from packaging, construction, domestic appliances. In contrast, PnBuA is a rubbery polymer ($T_g \sim -50^\circ\text{C}$), finding applications in, e.g., coating industry and as pressure sensitive adhesives.

Combination between PnBuA and PSty will therefore provide an interesting way to obtain melt-blends with a large range of physical properties. However, a compatibilization process is required to achieve a fine control of blend morphology, and therefore suitable properties. In this regard, the addition of CNTs to PSty or PnBuA is expected to modify the morphology of the resulting blends drastically. Indeed, nanofillers like CNTs were found to act as compatibilizers for immiscible polymer blends by selectively localizing at the interface of both polymers, reducing the coalescence phenomena.^[5] However, their confinement at the interface renders difficult an additional dispersion in one specific phase, and to take advantage of the functionalities/properties provided by these nanofillers. In this study, we report the possibility to specifically localize CNTs in selected polymer phases within polymer blends using imidazolium end-functionalized poly(styrene) (Im-PSty), poly(n-butyl acrylate) (Im-PnBuA) and even imidazolium end-functionalized poly(n-butyl acrylate-*b*-styrene) diblock copolymers as supramolecular compatibilizers.

Experimental Section

Materials

The multiwall carbon nanotubes were supplied by Nanocyl S.A. (Belgium) (Grade 7000). n-Butyl acrylate (nBuA, Acros, 99%) was purified by vacuum distillation (45 °C/18 mmHg). Styrene (Acros, 99 %) was purified by a filtration over Al₂O₃. Cu(I)Br (Aldrich, 98%) was purified by stirring with acetic acid, then by filtering and washing with ethanol and diethylether, and finally by drying in a vacuum oven at 70 °C. *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, Acros, 99 %) was distilled (85–86 °C/12 mmHg). Methyl 2-bromopropionate (MBP, Acros, 99%), 1-methyl imidazole (Merck, 99%), 11-bromoundecanol (Alfa Aesar, 97%), α -bromoisobutyryl bromide (Aldrich, 98%), bis(trifluoromethane)sulfonimide lithium (LiTFSI, Merck, 98%), methyl 2-bromopropionate (Aldrich, 98%) were used as received. Solvents were purchased from VWR (HPLC grade) and used without purification. All other chemicals were used as received.

Characterization

^1H NMR spectra were recorded in CDCl_3 at room temperature, with a Bruker Avance 300 spectrometer.

Size exclusion chromatography (SEC) was performed in THF/ NEt_3 (2 wt%) at 35°C using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate = $1\text{ mL}\cdot\text{min}^{-1}$), a Marathon autosampler (loop volume = $200\text{ }\mu\text{L}$, solution conc. = $1\text{ mg}\cdot\text{mL}^{-1}$), a PLDRI refractive index detector and three columns: a PL gel $10\text{ }\mu\text{m}$ guard column and two PL gel Mixed-B $10\text{ }\mu\text{m}$ columns.

Thermal gravimetric analyses (TGA) were recorded on a TA Instrument Q5000 purged with nitrogen flow, with a heating ramp of $20^\circ\text{C}\cdot\text{min}^{-1}$ from 20 to 800°C . Samples weight was generally in the range of 5 to 10 mg.

Matrix assisted laser desorption/ionization time of flight mass spectra (MALDI-TOF MS) were recorded on an Applied Biosystems Voyager DE STR MALDI-TOF spectrometer equipped with 2-m linear and 3-m reflector flight tubes and a 355-nm solid state UV laser (3.5-ns pulse). All mass spectra were obtained with an accelerating potential of 20 kV in positive ion mode and in reflector mode. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (BMPM) ($20\text{ mg}\cdot\text{mL}^{-1}$ in THF) was used as a matrix, and polymer samples were dissolved in THF ($2\text{ mg}\cdot\text{mL}^{-1}$). Analyte solutions were prepared by mixing $10\text{ }\mu\text{L}$ of the matrix, and $5\text{ }\mu\text{L}$ of the polymer solution. Subsequently, $0.5\text{ }\mu\text{L}$ of this mixture was spotted on the sample plate, and the spots were dried in air at room temperature. A poly(ethylene oxide) standard ($M_n = 2000\text{ g}\cdot\text{mol}^{-1}$) was used for calibration. All data were processed using the Data Explorer (Applied Biosystems) software package.

Transmission electron microscopy (TEM) was performed with a Philips CM200 with an acceleration voltage of 200 kV. Samples were prepared on a TEM grid by a simple drop casting procedure from a CNT/polymer solution. The excess of solution was removed by a filter paper whereupon the samples were stained with OsO_4 .

Atomic force microscopy (AFM) measurements were performed in ‘tapping-mode’ (TM-AFM). The cantilever holding the probe tip oscillates close to the resonance frequency (ca. 300 kHz) above the sample surface so that the tip is in intermittent contact with the surface at the lower end of the oscillation. Simultaneous recording of the phase and the height images provides a map of the local mechanical response. All TM-AFM images were recorded with a Nanoscope V microscope operated at room temperature in air using commercial cantilevers made of silicon with a spring constant of 30 N/m (Veeco). 512x512 pixels images were recorded, and the Nanoscope image processing software was used for image analysis. Unless otherwise stated, image treatment was limited to a ‘flattening’ operation, whereby a first-order surface representing height variations related to a possible tilt of the sample is subtracted from the original image.

Samples were prepared on a SiO₂ surface by a simple drop casting procedure from a CNT/polymer solution in CHCl₃

Synthesis of 1-(11-hydroxy-undecyl)-3-methylimidazolium bromide (1)

1-Methyl imidazole (4 mL, $50.4 \cdot 10^{-3}$ mol) and 11-bromoundecanol (13.9 g, $55.4 \cdot 10^{-3}$ mol) were stirred overnight in 4 mL of refluxing chloroform. Then, the oily residue was washed 3 times with diethylether to give the ionic liquid in 92 % yield. ¹H NMR (300 MHz, CDCl₃, δ): 9.83 (s, 1H, NCHN), 7.42 (t, 1H, CH=CH), 7.37 (t, 1H, CH=CH), 4.06 (t, 2H, OCH₂), 3.83 (s, 3H, NCH₃), 3.28 (t, 2H, NCH₂), 1.64 (m, 2H, CH₂), 1.24 (m, 2H, CH₂), 0.96 (m, 14H, CH₂).

Synthesis of 1-(11-(2-bromoisobutyryloxy)-undecyl)-3-methylimidazolium bis(trifluoromethane)sulfonamide (2)

1-(11-hydroxy-undecyl)-3-methylimidazolium bromide (2.6 g; $8 \cdot 10^{-3}$ mol) was dissolved in 40 mL of dichloromethane. To this solution, 2.9 mL α-bromoisobutyryl bromide ($24 \cdot 10^{-3}$ mol) was added dropwise. After stirring for 2 days at room temperature, the solvent was evaporated and the residual oil was washed 3 times with diethylether. Next, a solution of

bis(trifluoromethane)sulfonimide lithium salt (2.3 g; $8 \cdot 10^{-3}$ mol) in 40 mL of H₂O was added to the oil in order to change the counterion. After stirring the solution for 3 hours, the aqueous layer was extracted 3 times with CH₂Cl₂ (80 mL) and the organic phase is dried over Na₂SO₄. After evaporation of the solvent, the ATRP initiator was recovered with a yield of 73 %. ¹H NMR (300 MHz, CDCl₃, δ): 8.79 (s, 1H, NCHN), 7.30 (t, 1H, CH=CH), 7.27 (t, 1H, CH=CH), 4.13-4.19 (m, 4H, NCH₂ OCH₂), 3.95 (s, 3H, NCH₃), 1.92 (s, 6H, C(CH₃)₂), 1.27-1.88 (m, 18H, (CH₂)₉).

Synthesis of imidazolium containing homopolymers via ATRP

A typical polymerization procedure for the synthesis of Im-PnBuA homopolymers is as follows. A mixture of $55.9 \cdot 10^{-3}$ mol (8.0 mL) of the monomer nBuA, $0.28 \cdot 10^{-3}$ mol (0.19 g) of the initiator, $0.55 \cdot 10^{-3}$ mol (0.11 mL) of PMDETA, and 2.66 mL (25 vol%) of 1,4-dioxane was bubbled with N₂ for 30 min. to remove oxygen. Next, the reaction flask was immersed in an oil bath thermostated at 75 °C. When the reaction mixture reached the desired reaction temperature, the polymerization was started by adding $0.27 \cdot 10^{-3}$ mol (0.04 g) of Cu(I)Br under N₂ atmosphere. Samples were withdrawn periodically to monitor the monomer conversion (by ¹H NMR) and the average molecular weight (by SEC). The reaction was terminated by cooling the reaction mixture in liquid nitrogen. The resulting polymer was dissolved in THF and the copper catalyst was removed by passing the diluted reaction mixture over a column of Al₂O₃. After evaporating the excess of solvent, the polymer was precipitated in cold heptane (10-fold excess). For the synthesis of Im-PSty homopolymers, a similar procedure was followed as described above. However, in this case, no solvent was used during the polymerization, the reaction temperature was 105 °C, and the polymers were precipitated in methanol.

Synthesis of an imidazolium containing copolymer via ATRP

A mixture of $34.9 \cdot 10^{-3}$ mol (5 mL) of the first monomer (nBuA), $0.49 \cdot 10^{-3}$ mol (0.34 g) of the initiator, $0.99 \cdot 10^{-3}$ mol (0.21 mL) of PMDETA, and 1.66 mL of 1,4-dioxane (25 vol %) was bubbled with N_2 for 30 min to remove oxygen. Next, the reaction flask was immersed in an oil bath thermostated at 75 °C. When the reaction mixture reached the desired reaction temperature, the polymerization was started by adding $0.49 \cdot 10^{-3}$ mol (0.071 g) of Cu(I)Br under nitrogen atmosphere. Samples were withdrawn to monitor the monomer conversion (by ^1H NMR) and the average molecular weight (by SEC). After reaching 74% of conversion, $62.3 \cdot 10^{-3}$ mol (7.13 mL) of the second monomer (Sty), purged with N_2 , was added to the reaction solution. From here, the same procedure was followed as for the preparation of the Im-PnBuA and Im-PSty homopolymers. $M_n = 21400 \text{ g} \cdot \text{mol}^{-1}$; PDI = 1.17; composition = nBuA₅₂//nBuA₉/Sty₇₃ where the number before the double line indicates the average DP of the PnBuA segment before the addition of Sty, and the numbers after the double line indicate the composition second segment after the addition of Sty.

Synthesis of non-functionalized PnBuA and PSty homopolymers via ATRP

A mixture of $47.7 \cdot 10^{-3}$ mol (7.0 mL) of the monomer nBuA, $0.32 \cdot 10^{-3}$ mol (0.067 mL) of PMDETA, and 3.5 mL (33 vol%) of 1,4-dioxane was bubbled with N_2 for 30 min to remove oxygen. Next, Cu(I)Br ($0.32 \cdot 10^{-3}$ mol, 0.046 g) was added under N_2 atmosphere, and the reaction flask was placed in an oil bath at 75 °C. When the reaction mixture reached the desired reaction temperature, the polymerization was started by adding $0.32 \cdot 10^{-3}$ mol (0.035 mL) of MBP as the initiator. Samples were withdrawn periodically to monitor the monomer conversion (by ^1H NMR) and the average molecular weight (by SEC). The reaction was terminated by cooling the reaction mixture in liquid nitrogen (monomer conversion = 95%). The resulting polymer was dissolved in THF and the copper catalyst was removed by passing the diluted reaction mixture over a column of Al_2O_3 . After evaporating the excess solvent, the polymer was precipitated in cold methanol (10-fold excess). $M_n = 12900 \text{ g} \cdot \text{mol}^{-1}$; PDI = 1.35.

A similar procedure has been used for the preparation of a PSty homopolymer except that the monomer/ligand/catalyst/initiator ratio is 200/1/1/1 and the reaction temperature 100 °C. $M_n = 14100 \text{ g}\cdot\text{mol}^{-1}$; PDI = 1.21.

Dispersion tests

A solution of 100 mg Im-PnBuA or Im-PSty and 5 mg CNTs was stirred in 10 ml of chloroform overnight at room temperature. After cotton-filtration of the excess of CNTs, further characterization was performed as described below.

Results and Discussion

All ω -imidazolium (co)polymers were synthesized via atom transfer radical polymerization (ATRP) starting from an imidazolium functionalized ATRP initiator **2** that was prepared based on a literature procedure (scheme S1).^[6] First, an esterification reaction between a hydroxyl containing imidazolium salt **1** and α -bromoisobutyryl bromide yielded the corresponding ATRP initiator. Exchanging of the bromide counterion by bis(trifluoromethane)sulfonimide made this initiator soluble in organic media. The bromide containing initiator **2** was subsequently tested in the homopolymerization of nBuA (Figure 1; Table S1).

Figure 1. Homo- and copolymerization of nBuA and styrene via ATRP starting from an imidazolium containing ATRP initiator.

In all cases, PMDETA was used as ligand and the Cu(I)Br/PMDETA ratio was 1/2. This is slightly higher than the usual 1/1 ratio in ATRP because it is known that there can be a competition between PMDETA and the ‘ionic liquid’ initiator for the complexation with Cu(I).^[7]

When the reaction is performed in dioxane (25 vol %) at 75°C, high conversions could be obtained. The controlled character of the polymerization reaction is proved by the linear increase of the number average molecular weight (M_n) as a function of conversion, while the PDI remains narrow throughout the polymerization reaction (Figure 2, left). Except for the very beginning of the polymerization, also the first order kinetic plot shows a linear behavior, indicating a controlled reaction (Figure 2, right).

Figure 2: Homopolymerization of n-BuA. (Left) increase of M_n and evolution of PDI as a function of monomer conversion, (Right) first order kinetic plot.

MALDI-TOF MS analysis was carried out onto the purified polymers (Table 1, entries 2, 3 and 4) (Figure 3 (a)).

Figure 3: MALDI-TOF MS spectrum of PnBuA (Table 1, entry 2). (a) Complete spectrum, (b) Comparison of measured isotope distribution (top) and theoretical isotope distribution of $C_{19}H_{34}O_2N_2(C_7H_{12}O_2)_{40}Br$ (—) and $C_{19}H_{35}O_2N_2(C_7H_{12}O_2)_{41}$ (---) (bottom).

Upon comparison between the experimental and theoretical distributions (Figure 3 (b)), the main series (1) can be attributed to PnBuA with an imidazolium initiating group and a bromine end group.

Table 1: Molecular parameters of the (co)polymers synthesized via ATRP of n-butyl acrylate and styrene.

Entry ^a	Monomer	In. ^b	$M_{n,SEC}$ ^c	PDI ^c	$M_{n,MALDI}$
			[g·mol ⁻¹]		[g·mol ⁻¹]
1	nBuA	MBP	12900	1.35	N.D. ^d
2	nBuA	2	5000	1.16	5600

3	nBuA	2	11900	1.21	9600
4	Sty	MBP	14100	1.21	N.D. ^d
5	Sty	2	16400	1.25	15600
6	nBuA/Sty	2	21400	1.17	N.D. ^d

^a All reactions were carried out using Cu(I)Br as a catalyst and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) as a ligand; ^b MBP = methyl 2-bromopropionate; ^c THF-Et₃N as an eluent, relative to PSty standards; ^d Not determined.

Via ¹H NMR spectroscopy, it was shown that more than 90% of the polymer chains contained an imidazolium group.

Figure 4. Dispersions of CNTs in CHCl₃ in the presence of a) PnBuA, b) Im-PnBuA, c) PSty, and d) Im-PSty (see text).

The ATRP of styrene from the ‘ionic liquid’ initiator **2** has been performed in bulk at 105°C (Table 1, entry 5). The reaction mixture solidified after 2.4 hours for a DP_{theo} of 120. The polydispersity values indicate that also in this case, a controlled polymerization is obtained. MALDI-TOF analysis demonstrated that most polymer chains are functionalized with an imidazolium group. ¹H NMR analysis confirmed that more than 85% of all polymer chains were end-capped by an imidazolium cycle. The CNT dispersion ability of the imidazolium containing polymers was checked by simply mixing 100 mg of polymer with 5 mg of CNTs in 10 mL of chloroform and stirring overnight. After centrifugation, all dispersions -

independently of the molecular weight of the stabilizing polymer - remained stable over a period of three months (Figures 4 b and d).

Figure 5. TGA analysis of Im-PnBuA (Table 1, entry 3) and Im-PSty (Table 1, entry 5) as obtained from a chloroform suspension of CNTs after cotton-filtration and solvent evaporation, together with the analysis of the corresponding non-functionalized homopolymers. Inset: zoom over the TGA thermograms.

This indicates a strong interaction between the imidazolium end-groups and the CNTs. However, in order to discriminate with any other interaction from the polymer backbone, also some ‘blank’ dispersion tests were performed with the same polymer chains but not bearing any imidazolium end group. In the case of PSty, the CNTs completely sedimentated after a few seconds, showing that PSty backbone is not interacting at all with the CNTs (Figure 4 c). On the other hand, the CNT dispersion with PnBuA proved stable for a long time, even after centrifugation (Figure 4 a). This blank experiment reveals an interaction of the PnBuA chain with the CNTs in addition to the interaction with the imidazolium end-group.

A similar observation could be achieved via TGA analyses performed on the supernatant fraction recovered after cotton-filtration and complete removal of the chloroform from the various CNT dispersions (Figure 5). For the Im-PnBuA CNT dispersions, the residue at 500 °C after correction for the residual mass of the pure Im-PnBuA was approximately 1.7 wt%. By contrast, the residual mass for the Im-PSty CNT dispersions was only 0.5 wt%. Such behaviour indicates that Im-PnBuA is interacting much stronger with the CNTs, and by consequence is more efficient in solubilizing CNTs in CHCl_3 compared to Im-PSty. TGA

analysis of the ‘blank’ dispersion with PnBuA shows a residual mass of 0.4 wt% after the correction for the residual mass of the pure PnBuA (Figure 6).

Figure 6: TGA analysis of PnBuA as obtained from a chloroform suspension of CNTs after cotton-filtration and drying under vacuum together with the analysis of the corresponding pure homopolymers. Inset: zoom over the TGA thermograms from 400 to 600°C.

Such observation reveals an interaction of the polymer with the CNTs. In the case of PSty, an improved thermal stability was obtained in the presence of the CNTs since the CNT dispersions shows a different degradation profile compared to the corresponding homopolymer. No such effect could be observed in the case of PnBuA.

To visualize the dispersion ability of the different imidazolium containing polymers, an AFM analysis has been performed on the CNT suspensions (Figure 7). After solvent evaporation, a complete dispersion of the CNTs could be observed, both in the case of Im-PnBuA and Im-PSty, meaning that the imidazolium initiating group is able to break down the CNT aggregates. It should be noted that the resolution in AFM is somewhat lower in the case of the Im-PnBuA dispersions than for the Im-PSty dispersions because of the stickiness of the rubbery polyacrylate phase.

Figure 7: Tapping-Mode AFM phase images (2 μm x 2 μm) of drop cast a) Im-PnBuA/CNT and b) Im-PSty/CNT films on SiO_2 substrates.

Nevertheless, it seems that as a result of the additional interaction of the PnBuA backbone with the CNTs, Im-PnBuA is able to stabilize more CNTs compared to a dispersion with a similar amounts of Im-PSty, confirming the TGA analysis. Furthermore, no difference in morphology could be observed by changing the molecular weight of the stabilizing polymers.

Figure 8. TEM images recorded after solvent evaporation from a CNT dispersion in chloroform with a) a mixture of Im-PnBuA and Im-PSty (table 1, entries 3 and 5), and b) the Im-P(nBuA-b-Sty) block copolymer.

A TEM analysis has been performed on a CNT dispersion that was stabilized by a mixture of both imidazolium containing PnBuA and imidazolium containing PSty. Figure 8a shows that all CNTs are individualized by the imidazolium containing polymers. The diameter of the stabilized CNT is approximately 25-30 nm. Furthermore, the image evidences

that most CNTs are coated by Im-PnBuA as the CNTs are mainly situated in the PnBuA phase. Therefore, TEM demonstrates once again that the interaction of the CNTs with Im-PnBuA is much stronger than with Im-PSty. No CNTs specifically located at the interphase of the two polymer phases could be observed, indicating that the CNTs are only covered by one type of polymer. This can be explained by the immiscibility of these two homopolymers. Next, a CNT dispersion that was stabilized by an Im-P(nBuA-b-Sty) block copolymer, prepared via sequential comonomer addition, has been investigated via TEM (Figure 8 b).

Also in this case, the image revealed the complete dispersion of CNTs with the presence of individual CNTs confirming that the imidazolium containing polymer is able to dissociate the CNT bundles. Nevertheless, the CNTs were found to be located mainly in the PSty phase. Such behavior could be explained by the Im-PnBuA segment that is interacting with the CNTs. Therefore, the PSty segment is pointing towards the outside and forms a 'protective' layer around the CNTs, preventing the CNTs of locating within the PnBuA phase. In other terms, we are able to guide the localization of nanotubes towards a specific polymer phase upon the functionality and the structure of supramolecular polymeric surfactants.

Conclusion

In this work, the synthesis and CNT dispersion ability of imidazolium end-capped poly(n-butyl acrylate) and poly(styrene) is presented. These end-functionalized polymers were prepared in a controlled way via ATRP starting from an imidazolium containing initiator. In all cases, an efficient stabilization of CNTs could be obtained as a result of the non-covalent interaction with the imidazolium containing polymers. Though, Im-PnBuA was able to stabilize CNTs in a more efficient way than Im-PSty because of an additional interaction with the PnBuA chain. Finally, it was shown that by changing the type of stabilizing polymer, the nanotubes could be specifically located in different polymer phase. This highly selective

behavior opens possibilities to use these materials for applications with improved electrical conductivity or barrier properties.

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Imidazolium end-functionalized ATRP polymers as directing agents for carbon nanotube dispersion and confinement

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Scheme S 1: synthesis of the imidazolium containing ATRP initiator.

Table S1: Summary of reaction conditions, monomer conversions and molecular parameters of the homopolymers synthesized by ATRP of n-butyl acrylate and styrene.

Entry ^a	Monomer	In. ^b	$[\text{M}]_0/[\text{In.}]_0/$ $[\text{Cu}]_0/[\text{Ligand}]_0^c$	Solvent [vol %]	Temp. [°C]	Time [min]	Conv. ^d [%]	$M_{n,\text{theo}}^d$ [g·mol ⁻¹]	$M_{n,\text{SEC}}^e$ [g·mol ⁻¹]	PDI ^e	$M_{n,\text{MALDI}}^f$ [g·mol ⁻¹]
1	nBuA	MBP	150/1/1/1	Dioxane 33	75	Over night	78	14900	12900	1.35	N.D. ^f
2	nBuA	2	100/1/1/2	THF 60	60	Over night	44	6300	5000	1.16	5600
3	nBuA	2	100/1/1/2	Dioxane 25	75	Over night	86	11700	11900	1.21	9600
4	Sty	MBP	200/1/1/1	-	100	Over night	87	18100	14100	1.21	N.D. ^f
5	Sty	2	120/1/1/2	-	105	144	95	12500	16400	1.25	15600

^a All reactions were carried out using Cu(I)Br as a catalyst and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) as a ligand; ^b MBP = methyl 2-bromopropionate;

^c $[\text{M}]_0$, $[\text{In.}]_0$, $[\text{Cu}]_0$, and $[\text{ligand}]_0$ = initial concentration of monomer, initiator, copper catalyst, and ligand, respectively; ^d Calculated from ¹H NMR; ^e THF-Et₃N as an eluent, relative to PSty standards; ^f Not determined.

Table S2: Summary of reaction conditions, comonomer conversions and molecular parameters of the P(*n*BuA-*b*-Sty) copolymer via ATRP and sequential monomer addition starting from theimidazolium containing initiator **2**.

Entry ^a	[<i>n</i> BuA] ₀ /[Sty] ₀ /[In.] ₀ / [Cu] ₀ /[Ligand] ₀ ^b	Solvent [vol %]	Temp. [°C] ^c	Time [min] ^c	Conv. <i>n</i> BuA ^c ^d [%]	Conv. Sty [%] ^d	<i>M</i> _{n,theo} ^d [g·mol ⁻¹]	<i>M</i> _{n,SEC} ^e [g·mol ⁻¹]	PDI ^e
6	70/125/1/1/2	Dioxane 25	75-90	240-O.N.	74-87	58	16000	21400	1.17

^a All reactions were carried out using Cu(I)Br as a catalyst, *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) as a ligand, and **2** as an initiator; ^b [*n*BuA]₀, [Sty]₀, [In.]₀, [Cu]₀, and [ligand]₀ = initial concentration of *n*-butyl acrylate, styrene, initiator, copper catalyst, and ligand, respectively; ^c before the addition of the second monomer and at the end of the polymerization; ^d Calculated from ¹H NMR; ^e THF-Et₃N as an eluent, relative to PSty standards.