Submission to Macromolecular Rapid Communications
((please add journal code and manuscript number, e.g., DOI: 10.1002/macp.201100001))
Article type: Full Paper

Synthesis of clicked imidazolium-containing biosourced copolymers and application in carbon nanotube dispersion [a]

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New polyesters incorporating a variable quantity of imidazolium rings along the backbone are synthesized by Huisgen 1,3-dipolar cycloaddition ("click" reaction). Subsequently, the imidazolium-grafted copolymers reveal an efficient dispersing ability towards the carbon nanotubes (CNTs) through supramolecular interactions in organic media. Interestingly, these compounds offer a simple and reliable strategy to control the quantity of dispersed CNTs as a function of imidazolium content. This approach is particularly suitable for the elaboration of biosourced and biodegradable materials based on poly(butylene succinate) with high-performance properties.

Introduction

Carbon nanotubes (CNTs) combine a unique set of structural, mechanical, thermal and electrical properties, which is highlighted in technological application fields as diverse as electronic devices, sensors, filtration systems or therapeutic materials.[1] Therefore, the

[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.))

association of CNTs and a polymer matrix has attracted a great deal of attention for the formation of high-performance polymer nanocomposites. [2] However, these nano-objects are densely packed into agglomerates (bundles) due to strong intermolecular π-π interactions, and their high aspect ratio represents a major drawback for their fine dispersion ability. In order to overcome this issue, various strategies aiming at their disentanglement have been developed over the past decade and represent a prerequisite for enhancing the properties of CNT-based nanocomposites. [3] In this regard, the supramolecular approach relies on a wide array of non-covalent bonds available in the chemist's toolbox, i.e., π-π stacking, cation-π and charge transfer interactions. Compared to the covalent functionalization, the non-covalent strategy thereby arises as a more compelling pathway due to the preservation of the CNT's structure, its reliability and straightforwardness. [4]

Imidazolium-based ionic liquids (ILs) were found to be efficient dispersing agents for CNT.[5] Ionic liquids (ILs) have been the object of intense interest due to their unique intrinsic properties such as a high ionic conductivity, low vapour pressure and good thermal and chemical stability. These aspects have contributed to their application in varied technological fields with promising enhancements. Indeed, their ionic structure affords a strong adsorption onto the electron rich structure of CNTs through cation-π and/or π-π interactions, enabling good CNT disentanglements. On these lines, some of us have already shown that the incorporation of an imidazolium ring at the extremity of a poly(L-lactide) (PLLA) chain gave rise to a good and stable CNT dispersion in organic solvent. [6] As a continuation of our investigation on high-performance CNTs-containing (bio)materials, we decided to focus on a biosourced-based copolymer, namely poly(butylene succinate-co-butylene diethyl(methyl-2-propargyl) malonate) (PBSDEMPAM). PBS is a commercially available linear aliphatic polyester obtained by condensation of succinic acid (SuA) (or corresponding diesters) and 1,4-butanediol (BDO), very recently issued from renewable resources. [7] This polyester combines biodegradability and biocompatibility with thermal and mechanical properties

comparable to those of low-density polyethylene and polypropylene. [8] Interestingly, its possible range of applications can be modified by copolymerizing SuA and BDO with various functional comonomers. As far as PBSDEMPAM is concerned, the presence of triple bonds pending all along the polyester backbone offers a straightforward access to post-functionalization reaction by the Huisgen 1,3-dipolar cycloaddition ("click" reaction). Thus, we assumed that a "click" reaction with an appropriate ionic liquid could afford imidazolium ring-bearing PBSDEMPAM chains. The careful adjustment of pending group content could afford a modulation of anchoring sites towards the CNTs conjugated surface. Therefore, a fine tuning of CNTs dispersed quantity in solution is expected as a function of the relative imidazolium content.

Results and Discussion

Purposely, an ionic liquid functionalized by an azide group was prepared according to a three-step procedure starting from 1-(11-hydroxy-undecyl)-3-methylimidazolium bromide. [9] First, an esterification was performed with the 2-bromopropionyl bromide in chloroform followed by an anion exchange in the presence of bis(trifluoromethane)sulfonimide lithium salt (LiTFSI). Finally, the exchange of the bromide end-group against azide proceeded quantitatively via nucleophilic substitution with sodium azide in DMF at 60°C, providing the expected IL **1** (Figure 1).

Figure 1. Synthesis of ionic liquid **1** (IL **1**)

^{1}H NMR analysis confirmed the complete conversion into the azide derivative by the shift of the methyl group (N_3-CH(C$\underline{H}_3$)-) from 1.71 to 1.33 ppm and the proton in α position of the

azide group (N_3-C<u>H</u>(CH_3)-) from 4.66 to 4.29 ppm. In a second step, three different PBSDEMPAM **2** composed of variable quantities of pending propargyl units were synthesized by polycondensation of diethyl(methyl-2-propargyl) malonate (DEMPAM), [10] dimethyl succinate (DMSu) and BDO in the presence of titanium tetrabutoxide as catalyst ($Ti(OC_4H_9)_4$). The reaction proceeded in bulk condition at elevated temperature (160 to 200°C, see SI) to give, after treatment, the PBSDEMPAM **2a-c** in high recovery yields (Figure 2). As far as the molecular characterization is concerned, copolymers **2a-c** displayed number-average molecular weights (M_n) in the range from 4100 to 5500 g mol^{-1} and dispersities (Đ) from 1.58 to 2.13, as determined by size-exclusion chromatography (SEC) (Table 1).

Figure 2. Structure of PBSDEMPAM **2a-c** with propargyl group content from 5 to 17%

Further analysis by ^{1}H NMR spectroscopy revealed a DEMPAM unit content of 5, 10 and 17% in copolymers **2a-c**, respectively.

Table 1. molecular characteristic features of PBSDEMPAM **2a-c**

PBSDEMPAM	**Đ**	***M*n** **[a)]** **(g mol^{-1})**	**BDO/DMSu/DEMPAM ratio[b)]**
2a	1.58	5500	1/0.95/0.05
2b	2.13	5160	1/0.90/0.1
2c	1.94	4100	1/0.83/0.17

a) Determined by SEC in $CHCl_3$ at 35°C using an universal calibration
b) Determined by ^{1}H NMR spectroscopy

Subsequently, we focused on the 1,3-dipolar cycloaddition between PBSDEMPAM **2a-c** and ionic liquid **1**. In order to determine the effect of the relative quantity in imidazolium moieties on the CNT dispersion, an increasing amount of the cationic heterocycle was incorporated along the polymer chains by the cycloaddition reaction. Accordingly, the reactions were carried out with copper bromide (CuBr) as catalyst and pentamethyldiethylenetriamine (PMDETA) as ligand under conventional conditions, namely in THF at 50°C (Figure 3).

Figure 3. Synthesis of imidazolium-grafted PBSDEMPAM **3a-e** by "click" reaction

A clear and unambiguous confirmation of the successful coupling reaction was provided by ^{1}H NMR analysis. Indeed, the proton in α position of the azide group in IL **1** shifted from 4.29 ppm to 5.57 ppm and a new signal assigned to the proton of the triazole ring appeared at 7.92 ppm (see SI, Figure S1). The resulting polymers **3a-e** were thereby characterized by an imidazolium content ranging from 2 to 17%. The resulting imidazolium-grafted PBSDEMPAM **3a-e** presented number-average molecular weights from 2100 to 5900 g mol^{-1} with PDIs between 1.50 and 2.82 (Table 2).

Table 2. Characterization of imidazolium-grafted PBSDEMPAM **3**

PBSDEMPAM 2 (DEMPAM content)	**PDI[a)]**	***M*n [a)] (g mol^{-1})**	**imidazolium-grafted PBSDEMPAM 3 (imidazolium content)[b)]**

2a (5%)	1.50	5900	**3a** (2%)
	1.51	5600	**3b** (5%)
2b (10%)	2.19	3700	**3c** (9%)
2c (17%)	2.61	2500	**3d** (13%)
	2.82	2100	**3e** (17%)

a) Determined by SEC in $CHCl_3$ at 35°C using an universal calibration
b) Determined by ^1H NMR spectroscopy

Interestingly, M_n of compounds **3a-e** drastically decreased upon increasing the amount of anchored IL **1** and the associated Đ increased with respect to the ones of the starting copolymers **2a-c**. This variation is due to some tailing visible on the elution traces, which can be correlated to the high affinity of the cationic rings with the SEC columns. Indeed, this explanation is supported by the fact that M_w and M_p values remained unchanged. The imidazolium-grafted PBSDEMPAM **3a-e** were also characterized in terms of thermal properties by termogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Regarding the thermal stability (for representative example see SI, Figure S2), the incorporation of IL **1** pending along the chains allowed for retarding the thermal degradation of **2a-c** (difference of about 20 °C at 5 wt% weight loss), but did not influence the overall degradation rate. More remarkable was the IL **1** ascendency over crystallinity and crystallization rate (see SI, Figure S3). In all cases, T_c and T_m of **3a-e**, and the corresponding enthalpies (ΔH) shifted to lower values in comparison to **2a-c**. Clearly the presence of the bulky and charged substituent flanked along the polyester backbone decreased the crystallization rate and crystallinity. The effect was more pronounced at higher IL **1** amount (**3d** and **e**), resulting in complete disappearance of the crystallization exotherm upon cooling for **3e** (see SI, Table S1 and Figure S4). Meanwhile, a wide and poorly defined cold crystallization exotherm appeared upon heating. Besides, a shift in T_g and T_m to lower values was also observed, suggesting a plasticizing effect of the incorporated IL **1** and a disrupted crystallite structure, respectively.

Finally, the CNTs dispersion ability of copolymers **3a-e** was investigated through a simple visual test performed in chloroform. For comparison, the individual starting materials **1** and **2a-c** were evaluated as potential CNTs dispersing agents. 100 mg of **2a-c,** IL **1**, or **3a-e** were mixed in the presence of 5 mg of CNTs in 10 mL of $CHCl_3$. After overnight stirring at room temperature, the resulting **2a-c** solutions showed complete sedimentation of CNTs, explained by the absence of CNT anchoring groups along the polymer backbone. A similar result was obtained with a mixture of ionic liquid **1** and CNTs, even after several hours of vigorous stirring (Figure 4). This behavior has been reported recently.[6] In contrast to these results, when 100 mg of compounds **3a-d** were mixed with 5 mg of CNTs in 10 mL of $CHCl_3$, the resulting solutions revealed the formation of deeply black CNT dispersions, stable over a period of at least two months, i.e., CNTs sedimentation was not observed.

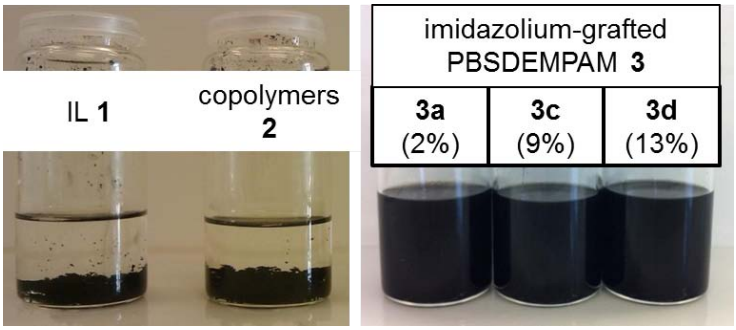

Figure 4. CNTs dispersion tests (in chloroform) with the ionic liquid **1**, copolymer **2** and imidazolium-grafted copolymers **3a,c,d** *(see Table 2)*

The remarkable dispersion ability of the imidazolium-grafted polyesters, even at IL content as low as 2%, is consistent with the occurrence of strong interactions between the imidazolium rings pending along the polyester backbone and the CNTs surface. It might therefore be supposed that the combined presence of "binding sites" (from the IL **1**) and the soluble polymer "carrier" (PBSDEMPAM) contribute to the successful CNTs dispersion. [11] Actually, an optimal balance between the relative content in "binding sites" and the length of the

polymer “carrier” has to be found out. For instance, the copolymer **3e**, thus containing 17% of IL **1**, did not display any ability for dispersing the nanotubes in chloroform. After vigorous stirring overnight, total CNT sedimentation was observed despite the fact that the compound incorporates the highest number of imidazolium “binding sites”. This is more likely explained by the low molecular weight of the polyester chain (M_n = 2100) and therefore the short distance in between successive IL “binding sites”.

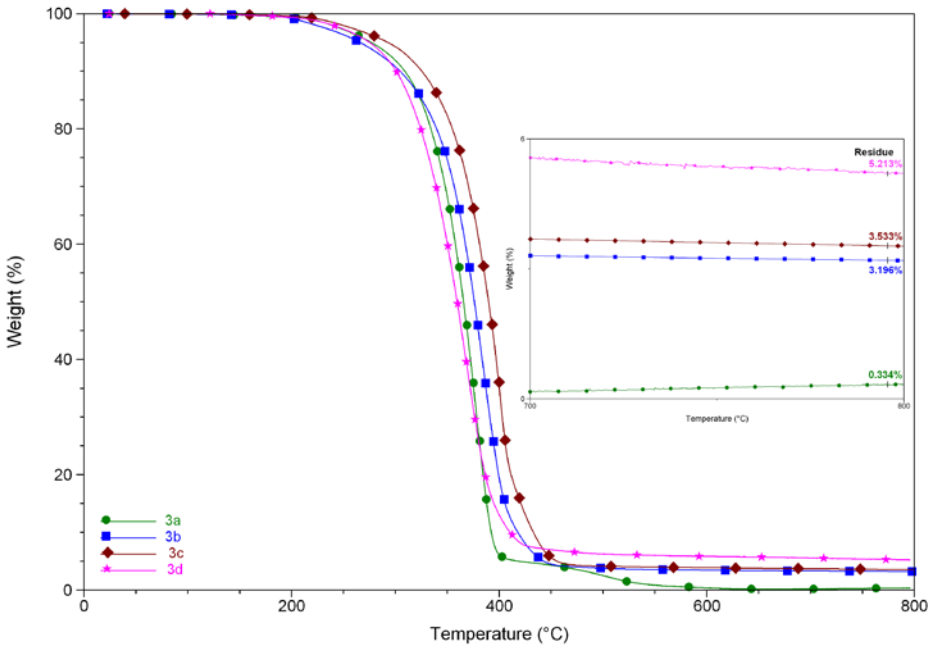

Figure 5. TGA analyses of imidazolium-grafted PBSDEMPAM **3a-d** as obtained from a chloroform suspension of CNTs after cotton-filtration

Interestingly, the binding affinity of polymers **3a-d** was further assessed by TGA analyses that have been performed onto the supernatant fraction as recovered after cotton-filtration of CNT-based suspensions in chloroform (Figure 5). After complete thermal degradation of the polymer chains, 0.3 to 5.2% materials were recovered, which corresponds to the CNT amounts initially trapped in chloroform by the imidazolium-grafted polyester. As expected, the quantity in nanotubes increased with the relative content in IL **1** pending along the copolymers **3a-d**.

Conclusion

In summary, we proposed a very appealing strategy aiming both at the dispersion and the control over the solubilized quantity of CNTs by means of imidazolium-grafted copolymers. In this regard, the synthesis of poly(butylene succinate-co-butylene diethyl(methyl-2-propargyl) malonate) incorporating variable amount of alkyne groups was performed by polycondensation. The subsequent "click" reaction between PBSDEMPAM and an azide-bearing ionic liquid gave rise to imidazolium-grafted copolymers with cationic ring contents ranging from 2 to 17% as evidenced by ^{1}H NMR. Then, their CNTs dispersion ability was evidenced in $CHCl_3$. The use of imidazolium-containing polymers thereby appears to be a reliable approach to the CNTs dispersion in organic media through supramolecular interactions. Moreover, the variation of the content in ionic liquid pending along the polymer backbone affords some fine tuning of the amount of polymer-anchored CNTs in reliable way for further preparation of CNT-based materials with high performance properties.

Acknowledgements: Financial support from Wallonia and European Commission (SINOPLISS-POLYEST) and OPTI²MAT program of excellence, by the Interuniversity Attraction Pole program of the Belgian Federal Science Policy Office (PAI 6/27) and by FNRS-FRFC is gratefully acknowledged.

Received: ((will be filled in by the editorial staff)); Revised: ((will be filled in by the editorial staff)); Published online: ((please add journal code and manuscript number, e.g., DOI: 10.1002/macp.201100001))

Keywords: carbon nanotubes; click reaction; ionic liquid; poly(butylene succinate); supramolecular interactions

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Alkyne-functionalized aliphatic polyester backbones were functionalized by various amounts of an imidazolium-based ionic liquid through “click” reaction. In solution, these polymers exhibited high binding ability towards carbon nanotubes with fine tuning of quantity of dispersed CNTs as a function of the imidazolium content.

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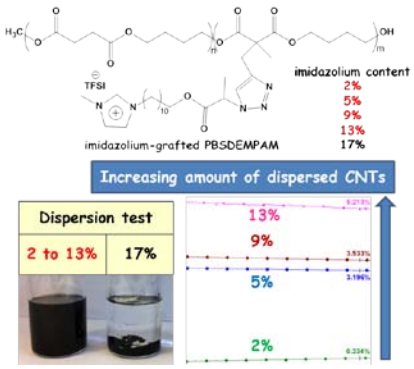
Synthesis of clicked imidazolium-containing biosourced copolymers and application in carbon nanotube dispersion



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Synthesis of clicked imidazolium-containing biosourced copolymers and application in carbon nanotube dispersion

Rosica Mincheva, Franck Meyer, Pierre Verge, Jean-Marie Raquez,* Leen Billiet, Filip Du Prez, Philippe Dubois*

Experimental Section

Materials.

The multi-wall carbon nanotubes (NanocylTM NC 7000) were supplied by Nanocyl S.A. (Belgium). These CNTs were produced via catalytic carbon vapour deposition (CCVD) process. 1-(11-hydroxy-undecyl)-3-methylimidazolium bromide was synthesized in our laboratory according to a procedure previously described in the literature. [1] Diethyl(methyl-2-propargyl)malonate (DEMPAM) was prepared according to the literature. [2] DMF, ether, dichloromethane and chloroform were purchased from VWR. Sodium azide, 2-bromopropionyl bromide, bis(trifluoromethane)sulfonimide lithium LiTFSI, magnesium sulfate were purchased from Aldrich. Dimethyl succinate (DMSu, MW = 146.14 g/mol, > 98 %, Kosher), 1,4-butanediol (BDO, MW = 90.12 g/mol, > 98 %, Kosher), diethyl methylmalonate (DEMMA, MW = 174.20 g/mol, 99 %, Across), hydroquinone (MW = 110.1 g/mol, 99 %, Fluka), propargyl bromide (MW = 118.96 g/mol, 80 wt.% stabilized in toluene, Aldrich) and tetrabutoxy titane (TBT, MW = 340.32 g/mol, 99 %, Across) were used as received. Copper(I) bromide (CuBr, MW = 143.45 g/mol, 98 %, Aldrich) was purified by stirring overnight with acetic acid, then by washing with ethanol and diethylether and drying under nitrogen and reduced pressure at r.t. to constant weight. *N,N,N',N',N''*-

pentamethylethylenetriamine (PMDETA, MW = 173.30 g/mol, > 99 %, Across) was distilled prior to use.

Characterization.

^{1}H spectra were recorded in DMSO-d_6 using a Bruker avance-500 apparatus. Size exclusion chromatography (SEC) of all (co)polymers was performed in $CHCl_3$ at 30 °C using a Agilent liquid chromatograph equipped with a Agilent degasser, an isocratic HPLC pump (flow rate = 1 mL/min), an Agilent autosampler (loop volume = 200 µL, solution conc. = 2.5 mg/mL), an Agilent-DRI refractive index detector and three columns: a PL gel 10 µm guard column and two PL gel Mixed-D 10 µm columns (linear columns for separation of MW_{PS} ranging from 500 to 10^6 g/mol). Polystyrene standards were used for calibration. Thermal gravimetric analyses (TGA) were recorded on a TA Instrument Q5000 purged with nitrogen flow, with a heating ramp of 20°C/min from 20 to 800°C. Samples weight was generally in the range of 5 to 10 mg. Differential scanning calorimetry (DSC) measurements were carried out with a DSC Q2000 apparatus from T.A. Instruments under nitrogen flow (heating rate 10 °C/min). The first heating run was considered to erase the thermal history of all samples. Thus, crystallization (T_c), cold crystallization (T_{cc}) and melting (T_m) temperatures and their corresponding enthalpies (ΔH) were acquired from the cooling and the second heating run in nonisothermal experiments.

Synthesis of 3-(11-((2-bromopropanoyl)oxy)undecyl)-1-methyl-1H-imidazol-3-ium bis(trifluoromethane)sulfonimide

1-(11-hydroxy-undecyl)-3-methylimidazolium bromide (5 g, 15 mmol) is stirred in 50 mL of chloroform at room temperature to obtain clear solution. 2-bromopropionyl bromide (5 mL, 45 mmol) is then added dropwise and the reaction is allowed to proceed overnight. Then, the solution is concentrated and the compound is precipitated in ether and washed 3 times with ether. Finally, the obtained orange oil is solubilized in 50 mL of water and the anion exchange is performed with LiTFSI (4.3 g, 15 mmol) during 3h. The compound is extracted 3 times

with dichloromethane and dried over magnesium sulfate to give the ionic liquid in pure form. Yield: 83%.

^{1}H NMR (DMSO-d_6, 500MHz) δ(ppm) = 9.09 (1H, s, C**H**), 7.75 (1H, s, C**H**=CH), 7.69 (1H, s, CH=C**H**), 4.66 (1H, q, *J* = 6.8 Hz, C**H**-CH_3), 4.14 (4H, m, C**H**$_2$-O, C**H**$_2$-N), 3.85 (3H, s, C**H**$_3$), 1.77 (2H, qt, *J* = 7 Hz, C**H**$_2$), 1.71 (3H, d, *J* = 6.8 Hz, C**H**$_3$), 1.59 (2H, qt, *J* = 7 Hz, C**H**$_2$), 1.25 (14H, m, C**H**$_2$).

Synthesis of ionic liquid 1

3-(11-((2-bromopropanoyl)oxy)undecyl)-1-methyl-1H-imidazol-3-ium bis(trifluoromethane)sulfonimide (8.4 g, 12.5 mmol) and sodium azide (2.44 g, 37.5 mmol) are stirred at 60°C in 35 mL of DMF overnight. Then, water is added and the compound is extracted 3 times with dichloromethane. The organic layer is washed 2 times with HCl 0.1M and dried over magnesium sulfate to give the ionic liquid in pure form. Yield: 92%.

^{1}H NMR (DMSO-d_6, 500MHz) δ(ppm) = 9.09 (1H, s, C**H**), 7.75 (1H, s, C**H**=CH), 7.69 (1H, s, CH=C**H**), 4.29 (1H, q, *J* = 7 Hz, C**H**-CH_3), 4.14 (4H, m, C**H**$_2$-O, C**H**$_2$-N), 3.85 (3H, s, C**H**$_3$), 1.77 (2H, qt, *J* = 7 Hz, C**H**$_2$), 1.60 (2H, qt, *J* = 7 Hz, C**H**$_2$), 1.34 (3H, d, *J* = 7 Hz, C**H**$_3$), 1.25 (14H, m, C**H**$_2$).

Synthesis of poly(butylenesuccinate-co-butylenemalonate) (P(BS-co-BDEMPAM))

The synthesis of P(BS-*co*-BDEMPAM) was performed by a two step melt polycondensation in a specially designed Inox® polycondensation reactor (Autoclave, France). The ratio DMSu/DEMPAM was varied in order to obtain copolymers of variable amounts of C≡C pendant groups. For example, the synthesis of P(BS_9-*co*-$BDEMPAM_1$) was performed as follows: 11.74 g (130 mmol, 1 eq) BDO, 17.12 g (117 mmol, 0.9 eq) DMSu and 2.58 g (13 mmol, 0.1 eq) DEMPAM were charged in a 50 ml polycondensation reactor. Then, 0.0136 g (4×10^{-5} mol, 3×10^{-4} eq/eq BDO) TBT was added via a syringe and the reaction proceeded for 130 min. and heated at 160 ºC under nitrogen flow during 150 min. The reactor temperature

was subsequently increased to 200 ºC with steps of 10 °C/10 min and vacuum was applied during 30 min while the reaction proceeds for 120 min more. The product was collected, cooled to r.t. and purified by dissolution in chloroform to homogenous solution, washing once with 0.1 M hydrochloric acid solution, then twice with demineralized water for complete catalyst extraction, and precipitation in 7 fold (v/v) excess of cold heptane overnight. The white precipitate was recovered by filtering and drying to constant weight at 40 °C under reduced pressure overnight. Yield: 94 %.

^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm) = 4.02 (4H, t, -OC**H**$_2$CH$_2$CH$_2$C**H**$_2$O-), 3.65 (3H, s, **H**$_3$CO-), 3.39 (2H, t, HOC**H**$_2$CH$_2$CH$_2$CH$_2$O-), 2.70 (1H, s, CH$_3$C(CO)$_2$CH$_2$C≡C**H**), 2.48 (4H, t, -C(O)C**H**$_2$C**H**$_2$C(O)-), 2.40 (2H, q(s), CH$_3$C(CO)$_2$C**H**$_2$C≡CH), 1.61 (4H, t, -OCH$_2$C**H**$_2$C**H**$_2$CH$_2$O-),1.43 (3H, t, C**H**$_3$C(CO)$_2$CH$_2$C≡CH).

*Synthesis of poly(butylenesuccinate-co-butylenemalonate)-g-ionic liquid 1 imidazolium-grafted PBSDEMPAM **3***

In this part, the “click” reaction between P(BS-*co*-BDEMPAM) and IL1 was performed via Huisgen 1,3-dipolar cycloaddition. In a round-bottom flask, equipped with a three-way stop-cock sealed with a rubber septum, and a magnetic stirrer, 0.0791 g (0.55 mmol, 1 eq) CuBr and 0.0949 g (0.55 mmol, 1 eq) PMDETA were charged and degassed by three consecutive freeze-thaw cycles. The as formed catalyst complex was dissolved in 10 ml dry THF. Meanwhile, 1 g (0.55 mmol, 1 eq C≡C) P(BS$_9$-*co*-BDEMPAM$_1$) and 0.3493 g (0.55 mmol, 1 eq N$_3$) IL1 were charged into a separate flame-dried round-bottom flask, dissolved with 15 ml dry THF and purged with nitrogen for 10 min. Once degassed, the obtained clear solution was transferred to the catalyst complex and the reaction was allowed to proceed under nitrogen at 50 °C for 24 h. The product was recovered by THF evaporation and dissolved in CH_2Cl_2 for purification. After the removal of Cu(I) and Cu(II) active complexes from the crude P(BS$_9$-*co*-BDEMPAM$_1$)-*g*-IL1$_9$ solution in CH_2Cl_2, the graft-copolymer was treated with 10 ml 0.1 M HCl aqueous solution and 2 × 10 ml distilled water. The P(BS$_9$-*co*-BDEMPAM$_1$)-*g*-IL1$_9$

was then collected by precipitation in 7-fold excess of cold heptane, filtration of the white precipitate and drying under reduced pressure at r.t. to constant weight. Yield: 93 %.

^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm) = 9.00 (1H, s, -NC**H**N-), 7.92 (1H, s, -CC**H**N-), 7.69-7.75 (2H, s, -NC**H**C**H**N-), 5.57 (1H, q, -NC**H**(CH_3)CO-), 4.02 (4H, t, -OC**H**$_2$$CH_2$$CH_2$C**H**$_2$O-; 2H, t, -OC**H**$_2$$CH_2$- from the IL1; and 2H, t, -CH_2C**H**$_2$N- from the IL1), 3.85 (3H, s, CH_3), 3.59 (3H, s, **H**$_3$CO-), 3.39 (2H, t, HOC**H**$_2$$CH_2$$CH_2$$CH_2$O-), 3.09 (2H, s, $CH_3C(CO)_2$C**H**$_2$C(N)=CH), 2.50 (4H, t, -C(O)C**H**$_2$C**H**$_2$C(O)-), 1.71 (3H, d, -NCH(C**H**$_3$)CO-), 1.61 (4H, t, -OCH_2C**H**$_2$C**H**$_2$$CH_2$O-), 1.27 (3H, m, -OCC(C**H**$_3$)(CH_2)CO-), 1.22 (14H, t, -C**H**$_2$- from the aliphatic chain of the IL1).

Typical procedure for the preparation of MWCNTs dispersion with imidazolium-grafted PBSDEMPAM 3

100 mg of imidazolium-grafted PBSDEMPAM **3a-e** and 5 mg of MWCNTs are stirred in 10 mL of $CHCl_3$ overnight. Then, the mixture was centrifuged at 4000 rpm for 10 mn.

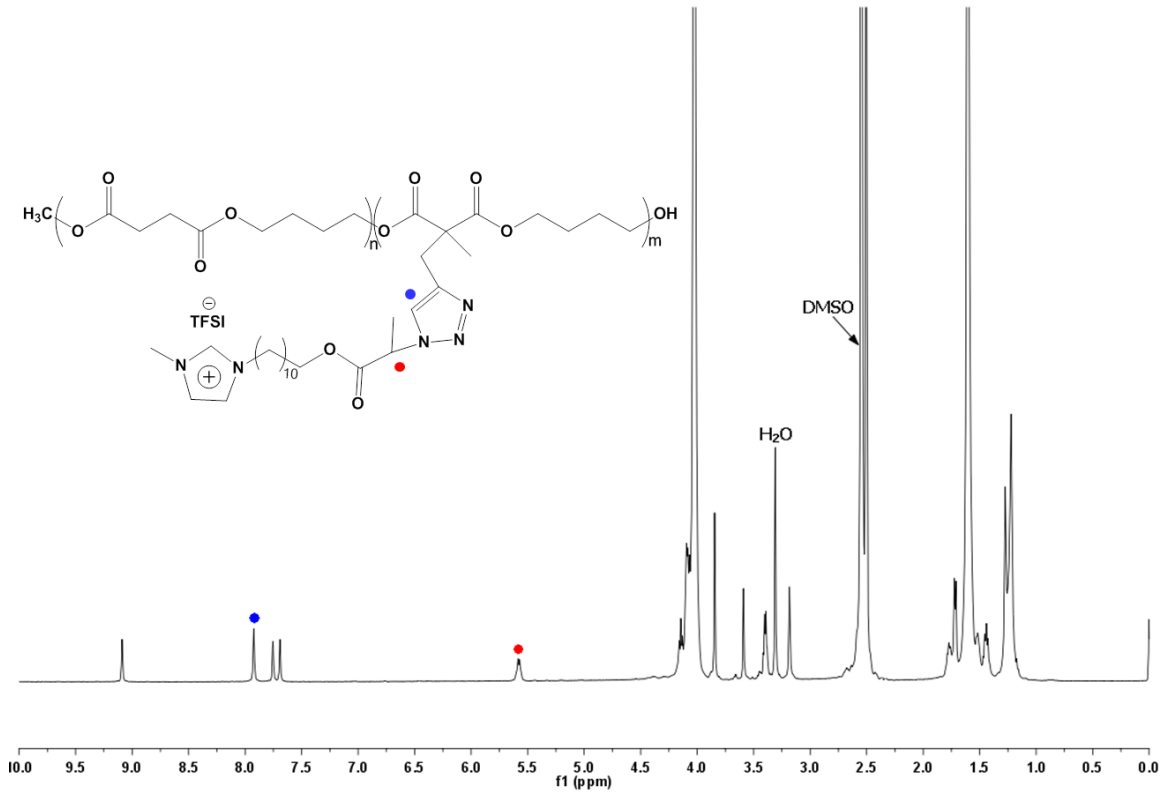


Figure S1. ^{1}H NMR spectrum of imidazolium-grafted PBSDEMPAM **3**

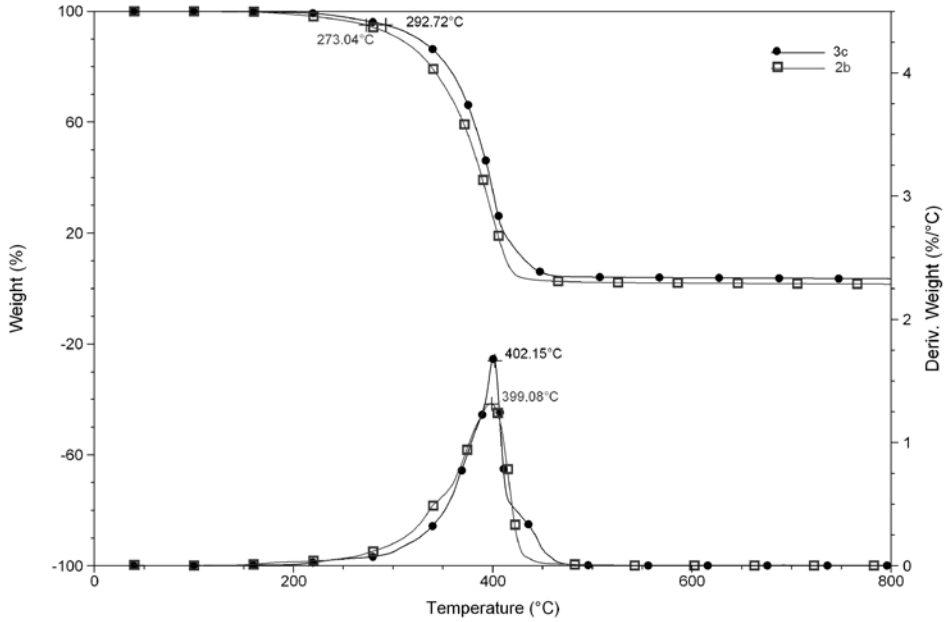


Figure S2. TGA thermograms of PBSDEMPAM **2b** and imidazolium-grafted PBSDEMPAM **3c**.

Table S1. Thermal properties of imidazolium-grafted PBSDEMPAM **3a-e**.

No	**Cooling run**		**2nd Heating run**		
	Tc (°C)	**ΔHc (J/g)**	**Tg (°C)**	**Tm (°C)**	**ΔHm (J/g)**
3a	72	68.04	-27	108	62.97
3b	67	62.02	-36	97/106	58.66
3c	53	52.33	-35	91/99	51.84
3d	26	32.41	-33	80	39.95
3e	n.v.	/	-33	85	2.375

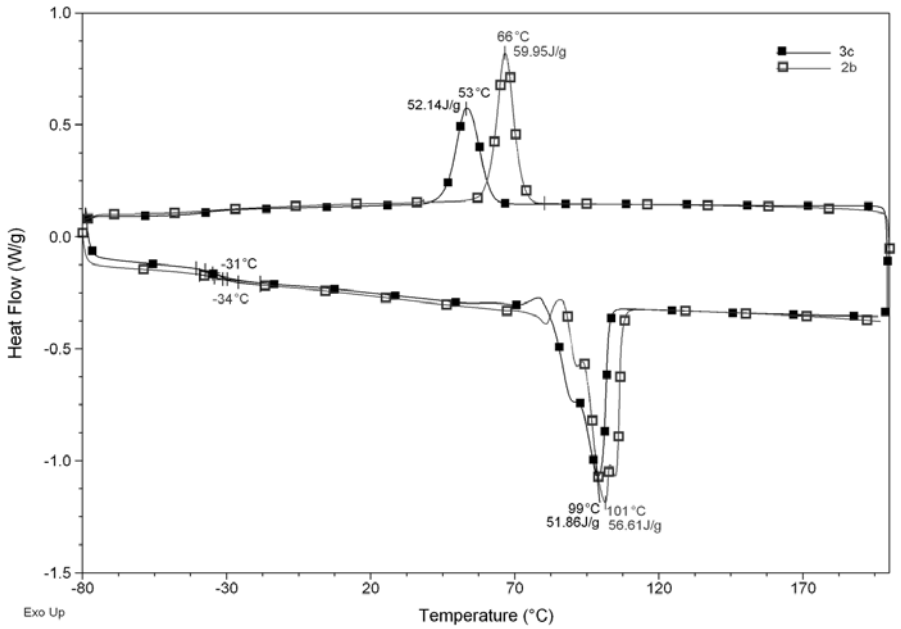


Figure S3. DSC thermograms of PBSDEMPAM **2b** and imidazolium-grafted PBSDEMPAM **3c**. Cooling and second heating runs.

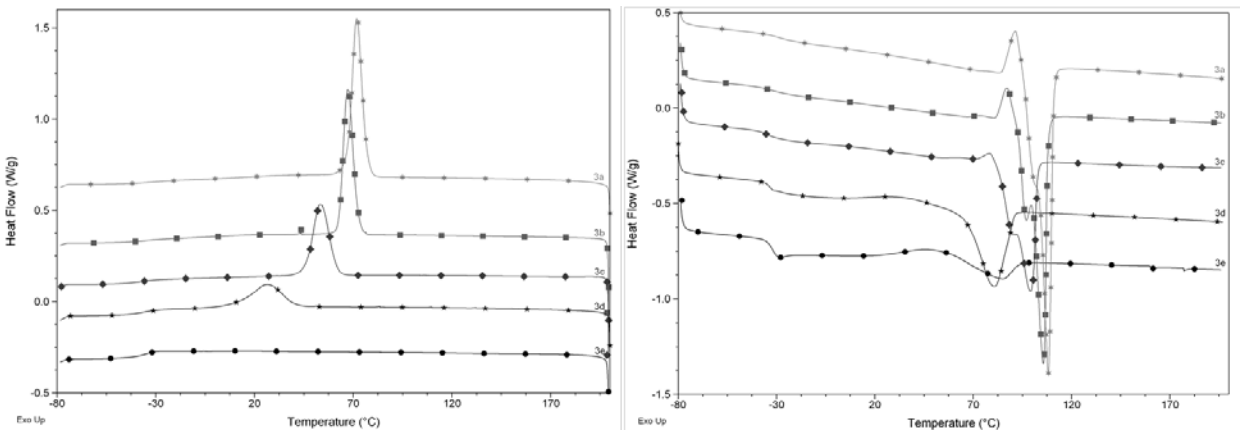
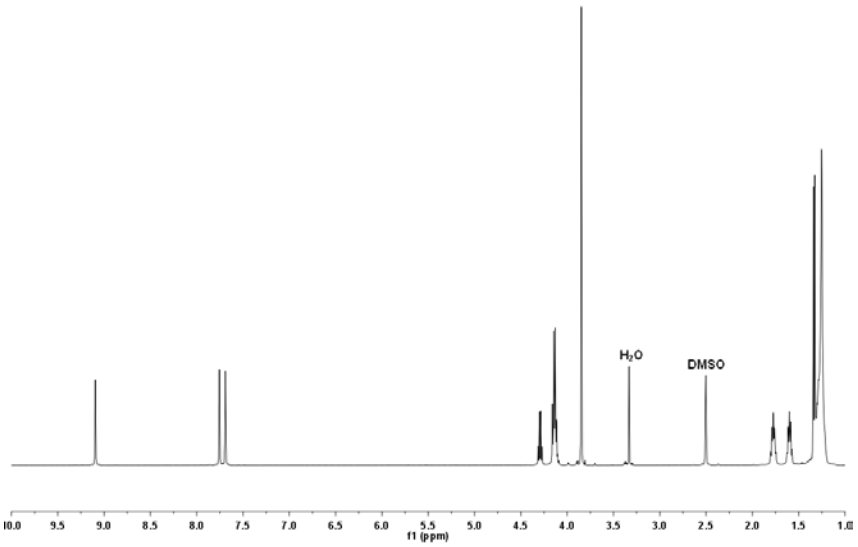


Figure S4. DSC thermograms of imidazolium-grafted PBSDEMPAM **3a-e** as a function of IL **1** amount. Cooling (left) and second heating (right) runs.

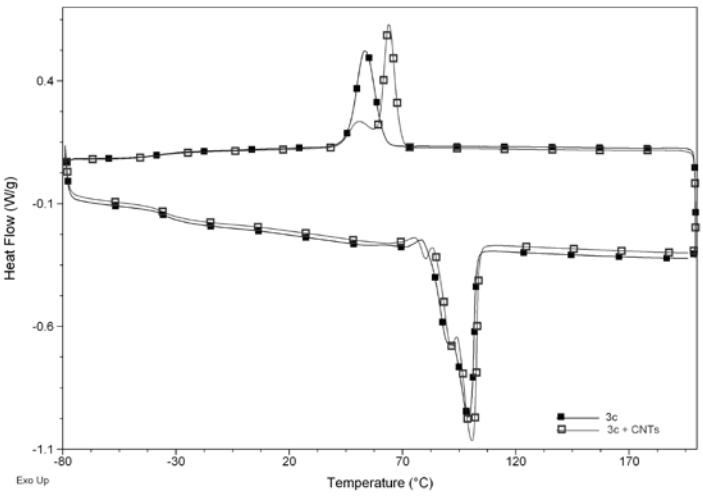


^{1}H NMR spectrum of ionic liquid **1**

Thermal properties of **3c**/CNTs

No	Cooling run		2nd Heating run		
	Tc (°C)	**ΔHc (J/g)**	**Tg (°C)**	**Tm (°C)**	**ΔHm (J/g)**
3c	53	52.33	-35	91/99	51.84
3c/CNTs	64/51	58.08	-35	80/92/101	55.61

DSC thermograms of **3c**/CNTs



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