One-pot synthesis of TBTA-functionalized coordinating polymers

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ABSTRACT

A one-pot method for the functionalization of polyvinylbenzyl chloride with a tris-(benzyltriazolylmethyl)amine (TBTA) ligand via the copper-catalyzed azide–alkyne cycloaddition reaction (CuAAC) is reported, where the ligand is constructed simultaneously with its attachment to the polymer backbone. A hydrophobic TBTA polymer as well as co-polymers containing TBTA ligands were also prepared to demonstrate the possibility of tailoring the properties of the polymers. The polymers were characterized with FT-IR and NMR spectroscopy, elemental analysis, contact angle measurement, differential scanning calorimetry and thermal gravimetric analysis. The metal coordinating properties of films prepared from the polymers was also demonstrated using X-ray photoelectron spectroscopy and their structures inspected by scanning electron microscopy.

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1. Introduction

Coordinating polymers, i.e. polymers functionalized with organic ligands that enable metal ion coordination, have found applications as scavenger reagents and as catalyst supports in organic synthesis [1–4]. Other uses include their employment as anti-microbial materials [5–10], for waste water treatment [10,11] and for the recovery of trace metal ions [10,12–15]. Metals ions such as Cu^+, Cu^{2+} and, Zn^{2+} are known for their anti-fouling effect and have been used for centuries to prevent marine biofouling [16–18]. In order to tune the metal interaction with the sea environment, different ligands can be used within the coating on the hull of marine vehicles. Coordinating polymers provide a unique opportunity to do so. For this reason, we have an interest in developing polymers functionalized with various ligands and to investigate different aspects of the interaction between metal ions and the coordinating environment of the polymeric ligand [19–23].

Both Cu^+ and Cu^{2+} ions are used in coatings and they are known to be efficient biocides when used in excessive amounts, but it has been suggested that Cu^+ is the form of copper ion that crosses biological membranes [24]. However, Cu^+ is unstable in aqueous media and rapidly disproportionates into a mixture of Cu^{2+} and metallic copper [25] unless stabilized by ligands [26,27]. As a part of our current research on marine anti-fouling coatings, we have focused on the preparation of a copper ion coordinating polymer which is also compatible with coating materials [19].

In 2004, Fokin et al. introduced a new ligand, tris-(benzyltriazolylmethyl)amine (TBTA) (Fig. 1) that has shown promising results with respect to the stabilization of both Cu^+ and Cu^{2+} ions in the reaction environment, without requiring an inert atmosphere or anhydrous conditions, while at the same time keeping the Cu^+ ions accessible for chemical reactions [28–30]. This ligand has been also grafted onto a swellable polystyrene–PEG copolymer backbone, making it applicable for heterogeneous catalysis [31,32]. Furthermore, a polymerizable monomer of the TBTA ligand has been prepared as a precursor to soluble catalyst supports for homogenous reactions, for applications where the heterogeneous catalyst supports cannot give the same activity [33,34].

Although polymerization is a feasible method to access coordinating polymers, polymerization procedures are sensitive to the presence and variations of the functional group in the monomer. Therefore, post-functionalization of polymers can in some cases be preferential to a polymerization strategy [35]. The copper-catalyzed azide–alkyne cycloaddition (CuAAC) [36,37] is an interesting tool for post-functionalization of different polymers [38–45]. Considering the limited solubility of many polymers, the CuAAC reaction and other click reactions [46] can play a significant role in post-modification of polymers due to their high efficiency

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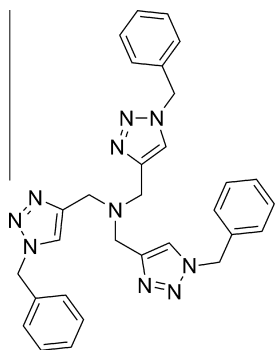E-mail addresses: Magnus.Nyden@unisa.edu.au (M. Nydén), kann@chalmers.se (N. Kann).

Fig. 1. Tris(benzyltriazolylmethyl)amine (TBTA), developed by Fokin et al. [28].

and tolerance to various solvents [35,47]. The CuAAC reaction has been widely applied in many different contexts [48]; nevertheless it is preferred not to isolate organic azide precursors due to safety issues [49]. This has led to the development of in situ methods for the nucleophilic displacement of halides with azide ion, followed by cycloaddition of the alkyne group to the substituted azide to form the 1,2,3-triazole ring with a 1,4-substitution pattern [50–54], or by using the ruthenium-catalyzed RuAAC reaction [55] to form the corresponding 1,5-substituted isomer [56].

Polyvinylbenzyl chloride (PVBC) is a commercially available polymer which reacts with nucleophiles via halide displacement and hence, has been found very useful in the synthesis of polymer supported reagents [57]. In this paper we describe a simple one-pot method for the functionalization of PVBC with TBTA-type ligands using the CuAAC reaction. The versatility of the CuAAC reaction also gives us the opportunity to attach other ligands to the polymer in the same manner to create different coordinating polymers. To demonstrate this, co-polymers containing both a TBTA unit and a *tert*-butyl-containing functionality were prepared using the same method. The effect of the structural variation in the different polymers was then evaluated using various techniques.

2. Experimental

2.1. Materials

Benzyl azide and polyvinylbenzyl chloride (PVBC), MW: 20,000–50,000 were obtained from Alfa Aesar and used as received. Remaining chemicals were purchased from Aldrich and used as received.

2.2. Characterization

The ^{1}H NMR spectra were recorded on an Agilent 400 MHz spectrometer using CDCl$_3$ as the solvent (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad). FTIR spectra were recorded on a Perkin Elmer system 2000 FTIR instrument (at a resolution of 2 cm^{-1} with 20 scans). Elemental analysis was carried out by Mikroanalytisches Laboratorium Kolbe (www.mikro-lab.de). Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA 7 (from room temperature to 500 °C at the rate of 20 °C/min). Differential scanning calorimetry (DSC) was performed on a Perkin Elmer Pyris 1 (Heating from 25 °C to 250 °C and cooling back to 25 °C with the rate of 10 °C/min, two cycles). Contact angle measurements were carried out using an Attention theta optical tensiometer (polymers drop-casted from CH$_2$Cl$_2$ solution onto a glass surface, triplicates for each sample with standard variation below 5%, static contact angle of de-ionized water against the surfaces). For Cu(II) ion absorption tests, two identical samples of each polymer were drop-casted onto a glass surface from a CH$_2$Cl$_2$ solution and left to dry overnight. One sample was then soaked in a

0.1 M CuSO$_4$ aqueous solution for 24 h, while the second sample was soaked in deionized water as a control sample. Each surface was subsequently rinsed thoroughly with deionized water and dried. These samples then were used for both imaging and XPS analysis.

2.3. Synthesis of ligand precursors 3a and 3b

Ligand precursor **3a** was prepared from benzyl azide, via intermediates **1a** and **2a**, following a procedure reported by Chan and Fokin [31]. Spectral data for **1a**, **2a** and **3a** were in accordance with reported data for these compounds. Compound **3b** was prepared via intermediates **1b** and **2b** as described below, using a modification of the route to **3a**, starting from 4-(*tert*-butyl)benzyl bromide.

2.3.1. 1-(4-(tert-Butyl)benzyl)-4-(diethoxymethyl)-1,2,3-triazole (1b)

In a 30 ml vial, 1-(bromomethyl)-4-(*tert*-butyl)benzene (1.0 g, 4.4 mmol), sodium azide (1.0 g, 15.4 mmol), and a catalytic amount of sodium iodide were dissolved in 15 mL of dimethylformamide (DMF). The reaction mixture was heated at 70 °C for 5 h. Water (20 mL) was then added followed by addition of diethyl ether (40 mL). The organic phase was washed with water (3 × 40 mL) to remove DMF. The solvent was removed under vacuum to yield a yellowish clear liquid. This crude product was used for the next step without any further purification.

The crude 1-(azidomethyl)-4-(*tert*-butyl)benzene was dissolved in a 1:1 mixture of *tert*-butanol and water (15 mL). To this solution, 3,3-diethoxy-1-propyne (0.51 g, 4.0 mmol) and sodium bicarbonate (0.40 g) were added. A CuSO$_4$ solution (0.10 M, 4.0 mL, 10 mol%) was added, resulting in a deep blue color. Upon the addition of sodium ascorbate (1.0 mmol, 0.20 g, 25 mol%) the solution again turned pale yellow. The mixture was stirred at room temperature for 48 h. Ethyl acetate (25 mL) was added and the organic phase was separated and washed with saturated NaHCO$_3$ solution (3 × 25 mL) and brine (25 mL), dried over MgSO$_4$ and concentrated under vacuum. The product was purified by flash chromatography on silica gel, using 20% ethyl acetate in heptanes as the eluent, affording the product as a white powder (0.895 g, 70%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49 (s, 1H, triazole—H), 7.42–7.36 (m, 2H, Ph—H), 7.24–7.18 (m, 2H, Ph—H), 5.69 (s, 1H, CH—O), 3.74–3.53 (m, 4H, O—CH$_2$), 1.32 (s, 9H, CH$_3$), 1.25–1.19 (t, 6H, CH$_3$); ^{13}C NMR (400 MHz, CDCl$_3$) δ 151.9, 147.4, 131.4, 127.9, 126.0, 121.7, 110.0, 96.9, 61.7, 53.9, 34.6, 31.2, 15.1.

2.3.2. 1-(4-(tert-Butyl)benzyl)-1,2,3-triazole-4-carbaldehyde (2b)

To a solution of **1b** (4.50 g, 14.2 mmol) in dichloromethane (45 mL), de-ionized water (15 mL) and trifluoroacetic acid (3.0 mL) were added and the solution was stirred at room temperature overnight. Ethyl acetate (50 mL) was added to the reaction mixture and the organic phase was washed with saturated NaHCO$_3$ (3 × 100 mL) and brine (100 mL), dried over MgSO$_4$ and the solvent removed under vacuum to give a white solid (3.21 g, 93%). Compound **2b** was used in the subsequent step without any further purification. ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.12 (s, 1H, CHO), 7.92 (s, 1H, triazole—H), 7.45–7.43 (m, 2H, Ph—H), 7.27–7.23 (m, 2H, Ph—H), 5.55 (s, 2H, CH$_2$), 1.32 (s, 9H, CH$_3$); ^{13}C NMR (400 MHz, CDCl$_3$) δ 185.1, 152.6, 130.2, 128.2, 126.4, 125.0, 110.0, 54.4, 34.7, 31.2; FTIR (KBr, cm^{-1}) ν 3440, 3116, 2957, 1922, 1702, 1613, 1533, 1466, 1437, 1417, 1242, 1161, 1107, 1047, 854, 791 and 561. Elemental analysis, calcd. for C$_{14}$H$_{17}$N$_3$O: C, 69.11; H, 7.04; N, 17.27. Found: C, 68.52; H, 7.05; N, 17.05

2.3.3. N,N-Bis((1-(4-(tert-butyl)benzyl)-1,2,3-triazol-4-yl)methyl)prop-2-yn-1-amine (3b)

Propargylamine (0.080 g, 1.4 mmol) and **2b** (0.71 g, 2.9 mmol) were dissolved in 20 mL of 1,2-dichloroethane. To this solution,

sodium triacetoxyborohydride (0.90 g, 4.2 mmol) was gradually added. The mixture was stirred at room temperature for 5 h until TLC analysis (silica, 80% ethyl acetate in heptane) showed no remaining starting materials. Water (20 mL) was then added, followed by addition of concentrated sulfuric acid (1.5 mL), stirring for 10 min to quench the excess of NaBH(OAc)$_3$. The solution was neutralized with aqueous K$_2$CO$_3$. The organic phase was separated and the aqueous phase was extracted with CH$_2$Cl$_2$ (3 × 20 mL). The combined organic phases were dried over MgSO$_4$ and the solvent was removed under reduced pressure. Flash chromatography on silica gel (80% ethyl acetate in heptane) gave a white solid powder (0.32 g, 46%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49 (s, 2H, triazole—H), 7.40–7.36 (m, 4H, Ph—H), 7.22–7.17 (m, 4H, Ph—H), 5.46 (s, 4H, Ph—CH$_2$), 3.83 (s, 4H, N—CH$_2$—triazole), 3.33 (s, 2H, N-CH$_2$-CCH), 2.23 (s, 1H, alkynyl—H), 1.31 (s, 18H, Ph—C—CH$_3$); ^{13}C NMR (400 MHz, CDCl$_3$) δ 151.8, 131.6, 127.9, 126.0, 123.0, 110.0, 54.4, 47.8, 45.5, 34.7, 31.2; FTIR (KBr, cm^{-1}) ν 3288, 2962, 2101, 1919, 1796, 1518, 1461, 1364, 1269, 1217, 1129, 1049, 1019, 963, 815, and 558. Elemental analysis, calcd. for C$_{31}$H$_{39}$N$_7$: C, 73.05; H, 7.71; N, 19.24. Found: C, 72.98; H, 7.74; N, 19.11.

2.4. General synthetic procedure for the one-pot functionalization of polyvinylbenzyl chloride (PVBC)

In a typical one-pot polymer functionalization reaction, a solution of PVBC (1.0 equiv, 0.31 g, 2.0 mmol chloride functionality), the ligand precursors (1.5 equiv for the homo-polymers; 0.75 equiv each of the ligand precursor and *tert*-butylacetylene for the co-polymers) and sodium azide (1.5 equiv) in DMF (7.5 mL per mmol of ligand precursor) was prepared at room temperature. To this solution, a CuSO$_4$ solution (10 mol%) was added whereupon the solution became brown. Sodium ascorbate (30 mol%) and de-ionized water (5 vol%) was added. At this point, the solution color gradually changed back to cloudy yellow. The temperature was then increased to 80 °C and the reaction was stirred for 48 h. The reaction mixture was then added dropwise into water (reaction solution:water, 1:10 v/v), after which the resulting suspension was centrifuged to afford the crude polymer. These steps were then repeated for purification, first with DMF and EDTA (1:10 of DMF:0.05 M EDTA in H$_2$O), and subsequently with CH$_2$Cl$_2$ and methanol (1:10 v/v CH$_2$Cl$_2$:MeOH). After the final centrifugation, the obtained product was dried under vacuum to afford the purified polymer as a powder.

2.4.1. Poly(tris[(1-benzyl-1,2,3-triazol-4-yl)methyl]amine) (4a) P(TBTA)

The product was obtained as a yellow powder (yield: 0.70 g, conversion *ca.* 60%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.64 (s, triazole-H), 7.24–5.90 (br m, Ph—H), 5.36 (br s, Ph—CH$_2$), 3.62 (br s, N—CH$_2$—triazole), 1.24 (br m, backbone carbons); FTIR (KBr, cm^{-1}) ν 3133, 2927, 2842, 1666, 1496, 1455, 1326, 1217, 1125, 1049, 819 and 720. Elemental analysis, Found: C, 67.13; H, 6.11; N, 23.35. Calculated loading: 1.67 mmol/g based on N content.

2.4.2. Poly(tris((1-(4-(tert-butyl)benzyl)-1,2,3-triazol-4-yl)methyl)amine) (4b) P(TtBBTA)

The product was obtained as a yellow powder (yield: 0.65 g, conversion *ca.* 50%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.66 (s, 3H, triazole-H), 7.24–6.00 (br m, 12H, Ph—H), 5.33 (br s, 6H, Ph—CH$_2$), 3.62 (br s, 6H, N—CH$_2$—triazole), 1.18 (br m, 21H, Ph—C—CH$_3$ and backbone carbons); FTIR (KBr, cm^{-1}) ν 3135, 2961, 2867, 1666, 1514, 1459, 1326, 1268, 1218, 1128, 1049, 815, 717 and 559. Elemental analysis, Found: C, 69.59; H, 6.91; N, 20.04. Calculated loading: 1.43 mmol/g based on N content.

2.4.3. Poly(4-(tert-butyl)-triazole-co-TBTA) (5a) P(tBT-co-TBTA)

The product was obtained as a yellow powder (yield: 0.54 g). ^{1}H NMR (400 MHz, CDCl3) δ 7.65 (s, triazole—H), 7.24–6.00 (br m, Ph—H), 5.40 (br s, Ph—CH$_2$), 3.65 (br s, N—CH$_2$—triazole), 1.21 (br m, Ph—C—CH$_3$ and backbone carbons); FTIR (KBr, cm^{-1}) ν 3133, 2928, 2846, 1668, 1606, 1455, 1326, 1218, 1124, 1053, 799 and 721. Elemental analysis, Found: C, 67.77; H, 6.28; N, 22.11. Calculated loading for each of the functionalities: 0.63 mmol/g based on N content, assuming a ligand ratio of 1:1 as determined by ^{1}H NMR.

2.4.4. Poly(4-(tert-butyl)-triazole-co-TtBBTA) (5b) P(tBT-co-TtBBTA)

The product was obtained as a pale yellow powder (yield: 0.62 g). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.67 (s, triazole—H), 7.24–6.00 (br m, Ph—H), 5.37 (br s, Ph—CH$_2$), 3.66 (br s, N—CH$_2$—triazole), 1.22 (br m, Ph—C—CH$_3$ and backbone carbons); FTIR (KBr, cm^{-1}) ν 3134, 2961, 2867, 1668, 1610, 1513, 1459, 1363, 1326, 1219, 1128, 1049, 815, 792, 703 and 559. Elemental analysis, Found: C 69.54, H 7.14, N 19.21. Calculated loading for each of the functionalities: 0.54 mmol/g based on N content, assuming a ligand ratio of 1:1 as determined by ^{1}H NMR.

## 3. Results and discussion

3.1. Synthesis of ligand precursors and functionalization of polyvinylbenzyl chloride

A TBTA-ligand precursor (**3a**, Scheme 1) containing two triazole unit and a pendant alkyne functionality was prepared in three steps via intermediates **1a** and **2a**, starting from commercially available benzyl azide and following a procedure reported by Chan and Fokin [31]. Moreover, a *tert*-butyl substituted version of the same precursor (**3b**, Scheme 1), with potentially higher solubility in organic solvents, was also prepared using a similar but slightly modified synthesis. The higher hydrophobicity of the *tert*-butyl substituted ligand could translate into better compatibility with oil-based paints, of importance for the ultimate goal of this project which is to develop marine coatings with antifouling properties. To access compound **3b**, 4-(*tert*-butyl)benzyl chloride was converted into the corresponding azide. Extensive purification of the intermediate azide was avoided in order to minimize risks involved with the handling of this reactive compound. This intermediate aryl azide was subsequently subjected to a CuAAC reaction with 3,3-diethoxy-1-propyne to form triazole **1b** in 70% yield. Deprotection of the acetal functionality with trifluoroacetic acid then afforded aldehyde **2b** in 93% yield, of sufficiently high purity to be used directly in the next step. Reductive amination with propargyl-amine, using sodium triacetoxyborohydride as the reducing agent, then provided the desired ligand precursor **3b** as a white solid in a moderate yield (46%).

The alkyne handle provides an opportunity to 'click' precursors **3a** and **3b** onto an azide-functionalized polymer while simultaneously installing the third triazole ring needed to complete the TBTA-structure of the ligand. To functionalize PVBC, a one-pot two-step synthetic pathway was developed (Scheme 2). A solution containing PVBC, the ligand, sodium azide and copper(II) sulfate was prepared. Although CuAAC reactions in many cases proceed at room temperature, a higher temperature (80 °C) was chosen in order to facilitate the nucleophilic substitution of halide with azide. In the first reaction step, PVBC was substituted with azide ion to form polyvinylbenzyl azide (PVBAz). In the second step, a CuAAC reaction between the supported azide functionality and the pendant alkyne on the ligand both provides the third triazole group needed for the formation of the TBTA-type structure, and simultaneously attaches the ligand to the polymer backbone.
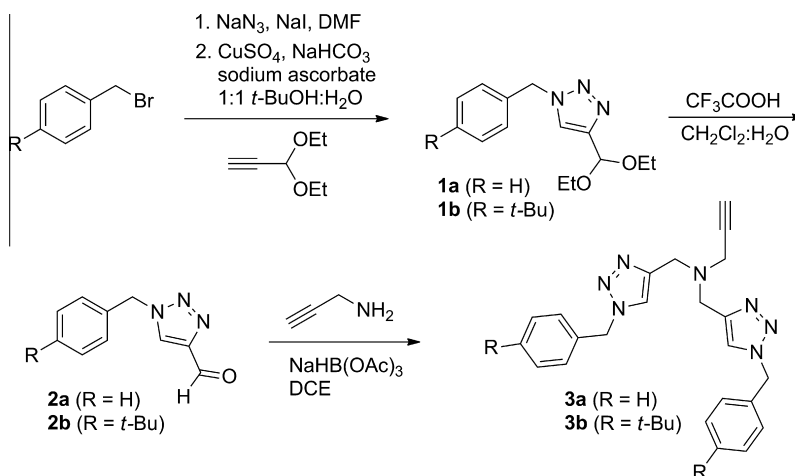
Scheme 1. General synthetic route for the preparation of TBTA-type ligand precursors **3a** and **3b**. Compound **1a** was prepared directly from benzyl azide.
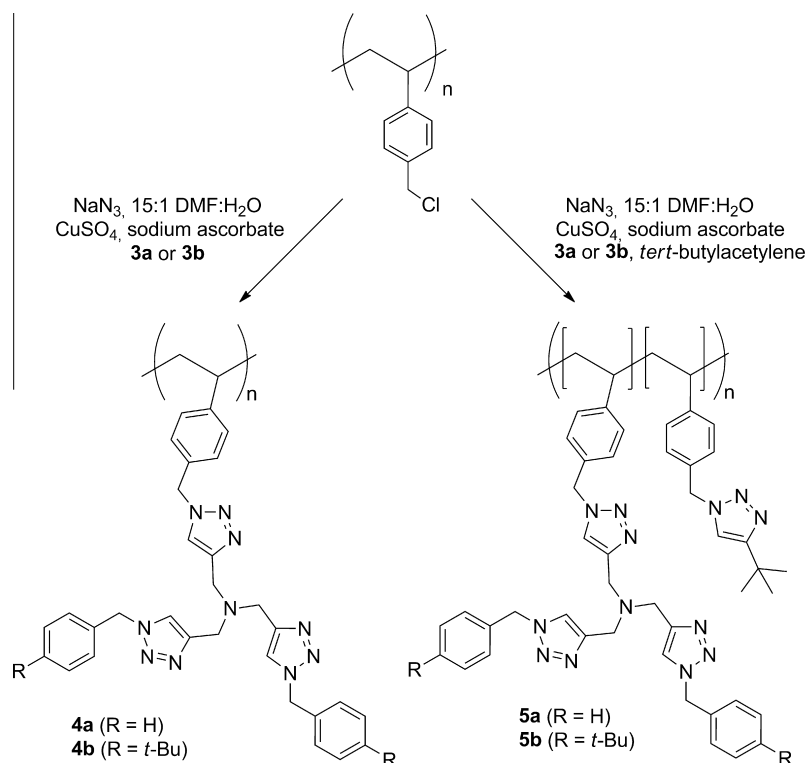
Scheme 2. General synthetic route for the one-pot functionalization of polyvinylbenzyl chloride (PVBC) with TBTA-type ligands.

Dimethylformamide (DMF), one of the commonly used polar solvents for the formation of alkyl azides from alkyl halides, was found to dissolve both PVBC and the ligands used in our experiments and was thus selected as a suitable solvent. A small amount of water was also added to facilitate the solution of copper sulfate and sodium ascorbate.

To prepare the TBTA-functionalized PVBC, equimolar amounts of Cl in the polymer and the ligand precursors **3a** and **3b** were initially used in the CuAAC reaction. FT-IR analysis of the isolated polymer product indicated that unreacted azide groups remained on the backbone, however. Applying a 50% excess of the ligand instead, afforded functionalized polymers **4a** and **4b** with no trace of any azide peak in FT-IR, indicating a complete reaction. To prepare co-polymers **5a** and **5b**, a 1.5-fold excess of a 1:1 mixture of the two ligand precursors was added to one equivalent of polymer.

Although the smaller of the two ligand moieties might be expected to dominate in the final polymeric materials, ^{1}H NMR spectra showed that the copolymers contained approximately equal amounts of the TBTA-type ligand and the simple *tert*-butyl triazole moiety.

Purification of the final polymers was achieved by re-precipitation in water to remove residual salts from the mixture, followed by a second re-precipitation in an EDTA solution to complex any remaining copper ions. The polymers were finally re-precipitated in methanol to remove unreacted ligand as well as potential organic side products, affording the desired materials as white solids after centrifugation and drying under vacuum.

The loading of the ligands on the polymer backbone was calculated from the nitrogen content determined via elemental analysis. Polymer **4a**, with the simple TBTA-ligand structure, showed the

highest loading (1.67 mmol/g) while **4b**, with the more sterically hindered *tert*-butyl substituted ligand afforded a slightly lower loading (1.43 mmol/g). For the co-polymers **5a** and **5b**, a ligand ratio of 1:1 affords loading values of 0.63 and 0.54 mmol/g. The lower values are expected in this case as the TBTA-type ligands are diluted by the smaller triazole unit also contained in the polymers. In this case also, the polymer with the highest degree of *tert*-butyl substituted moieties (i.e. **5b**) afforded the lower loading, most likely for steric reasons.

The solubility of the ligands was investigated in dichloromethane and ethyl acetate. All four ligands were found to be soluble in dichloromethane (5 mg/mL). At the same concentration in ethyl acetate, polymer **4b** and co-polymer **5b**, where all ligand moieties contain a *tert*-butyl group, were found to be fully soluble. Co-polymer **5a**, which contains a mixture of non-derivatised TBTA ligand and smaller *tert*-butyl substituted triazole units, was partially soluble in the same solvent, while the pure TBTA polymer **4a** was found to have very limited solubility. Tailoring of the ligand structure was thus found to be important for increasing the solubility in the environmentally more friendly solvent ethyl acetate. This factor can be beneficial for later applications of the polymers if one desires to limit the use of chlorinated solvents.

3.2. FT-IR analysis

FT-IR measurements were carried out to confirm the attachment of the ligand to the polymer backbone. The disappearance of the azide peak at 2100 cm^{-1} in the final polymers indicates complete conversion of the azide functionality on the polymer backbone into a triazole ring via the CuAAC reaction. Fig. 2 shows FT-IR spectra for polymers **4** and **5**. As expected, the spectra are quantitatively similar, although the —CH region at 3100 cm^{-1} is slightly more pronounced for the *tert*-butyl-containing polymers.

The tertiary amine bond is responsible for the signals in the 1200 cm^{-1} region. The region between 1670 cm^{-1} and 1600 cm^{-1} not only represents the aromatic C—C bonds in the phenyl ring, but also heterocyclic C=N. The broad peak in this region indicates the presence of 1,2,3-triazole moieties in the final polymer, and is thus an indirect proof of the attachment of the TBTA-ligand to the polymer (see Supporting information).

3.3. ^{1}H NMR analysis

The chemical structures of the four polymers were further confirmed by ^{1}H NMR, using CDCl$_3$ as the solvent. Fig. 3 shows the ^{1}H NMR spectra for P(TBTA) (**4a**) and P(T*t*BBTA) (**4b**). The relative integrals of the individual peaks are in good agreement with the expected values for the functionalized polymers (see experimental

Fig. 2. FT-IR spectra of polymers **4**–**5**.

section). The spectra of P(T*t*BBTA) shows a strong signal for the *tert*-butyl group at 1.18 ppm, while remaining peaks for the triazole rings, aromatic groups and benzyl moieties appear approximately at the same chemical shifts in the two polymers.

Fig. 4 shows the ^{1}H NMR spectra of the co-polymers P(*t*BT-*co*-TBTA) (**5a**) and P(*t*BT-*co*-T*t*BBTA) (**5b**). The integration of the *tert*-butyl region and the N—CH$_2$—triazole protons gives the proportions of the two different ligands in the polymer, resulting in approximately a one-to-one ratio of the *tert*-butyl triazole to TBTA-ligand for both polymers, corresponding well to the expected ratio considering that equimolar amounts of the ligand precursors and *tert*-butylacetylene were used in the synthesis.

3.4. Contact angle measurements

To compare the hydrophobicity, the four different polymers were dissolved in CH$_2$Cl$_2$ and drop-casted onto a glass substrate and left to dry over night. The contact angle of de-ionized water was then measured (see Table in Supporting information). A higher contact angle was observed for the polymers carrying a *tert*-butyl group (**4b**, **5a** and **5b**), indicating a higher degree of hydrophobicity. The least hydrophobic polymer in the series was P(TBTA) (**4a**) with a contact angle of 67° and the most hydrophobic polymer was P(T*t*BBTA) (**5b**) with a 81° contact angle, with **5a** and **5b** showing intermediate values. The contact angle experiments demonstrate that the hydrophobicity of the polymers can be fine-tuned by mixing the two functional groups.

3.5. Differential scanning calorimetry (DSC) analysis

DSC measurements were carried out to analyze the glass transition temperature (T_g) of the polymers (Fig. 5). The P(TBTA) polymer **4a** displays no change in the temperature region between 25 °C and 250 °C, however the *tert*-butyl containing polymers show a distinct shoulder in the same temperature range (82–105 °C) which represents their glass transition temperature (T_g).

3.6. Thermal gravimetric analysis (TGA)

Fig. 6 shows the thermal stability of the polymers as measured by thermal gravimetric analysis. The measurements show that all of the functionalized polymers are thermally stable up to 340–350 °C.

3.7. Polymer thin film characterization and determination of copper uptake using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS)

To demonstrate the function of these polymers in terms of their ability to absorb copper ions, thin films were prepared by drop-casting solutions of the polymers onto a glass surface, as described in Section 2.2. The structures of the films were inspected by optical microscopy as well as scanning electron microscopy. The copper content was monitored using X-ray photoelectron spectroscopy. Table 1 presents the elemental composition of the polymer films measured by XPS. PVBC is the only sample which shows any Cl content. The lack of Cl in the functionalized polymers **4a**, **4b**, **5a** and **5b** confirms that all the chlorine atoms have been substituted during the functionalization reaction. Moreover, the PVBC sample showed no copper content after immersion in the Cu(II) solution for 24 h. All of the functionalized polymers have absorbed copper from the CuSO$_4$ solution. The copper content is the highest for P(TBTA) (**4a**) in comparison with the other functionalized polymers. Also, P(TBTA) (**4a**) is the only sample where the appearance of the polymer changes substantially upon copper coordination.
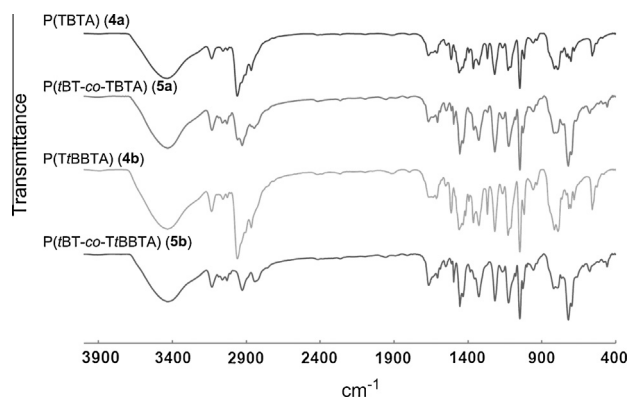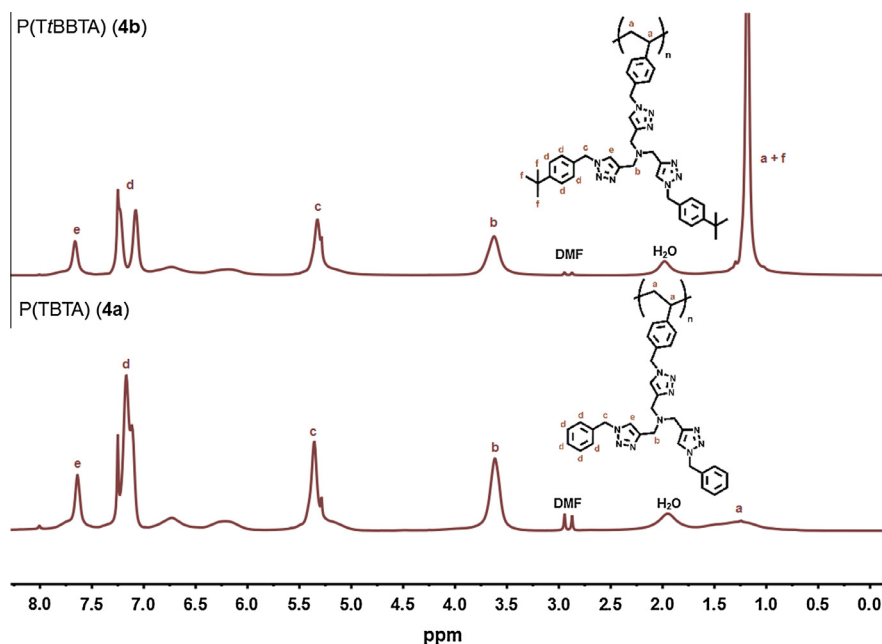
Fig. 3. ^{1}H NMR spectra of P(TBTA) (**4a**) and P(TtBBTA) (**4b**).
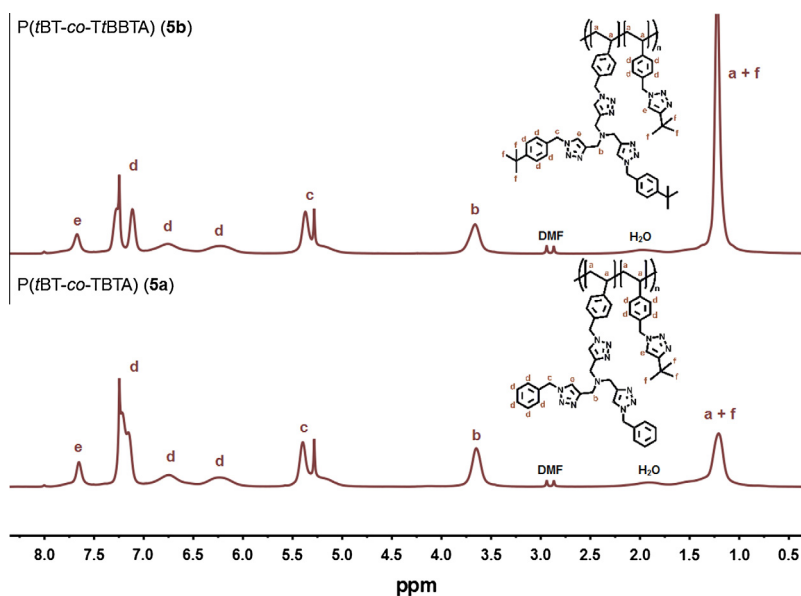

Fig. 4. ^{1}H NMR spectra of co-polymers P(tBT-co-TBTA) (**5a**) and P(tBT-co-TtBBTA) (**5b**).
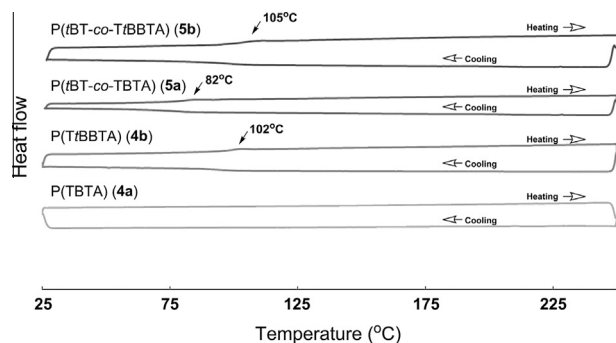

Fig. 5. Results from the differential scanning calorimetry (DSC) of the polymers. The arrow shows the glass transition temperature in each case.

For the homo-polymers **4a** and **4b**, assuming that each repeating ligand unit of the polymer binds to one copper ion, the theoretical ratio of Cu/N should be around 10%. This is almost the case for P(TBTA) (**4a**) with a Cu/N ratio of 8%. For P(TtBBTA) (**4b**), the Cu/N ratio is 5% which is half of the theoretical value. For co-polymers **5a** and **5b**, the coordinating behavior of the polymers is more complicated to predict as both the TBTA-type ligands as well as the mono-triazole units can bind to copper. In general, the different behavior of the polymers in terms of stabilizing copper from the solution can be explained both by their different coordinating preferences, and also by their difference in the hydrophobicity which can hinder the access of copper ions in the aqueous solution to the coordinating sites within the coating.

Upon drop-casting, PVBC is able to form a continuous and uniform film which is transparent. The appearance of this film stays
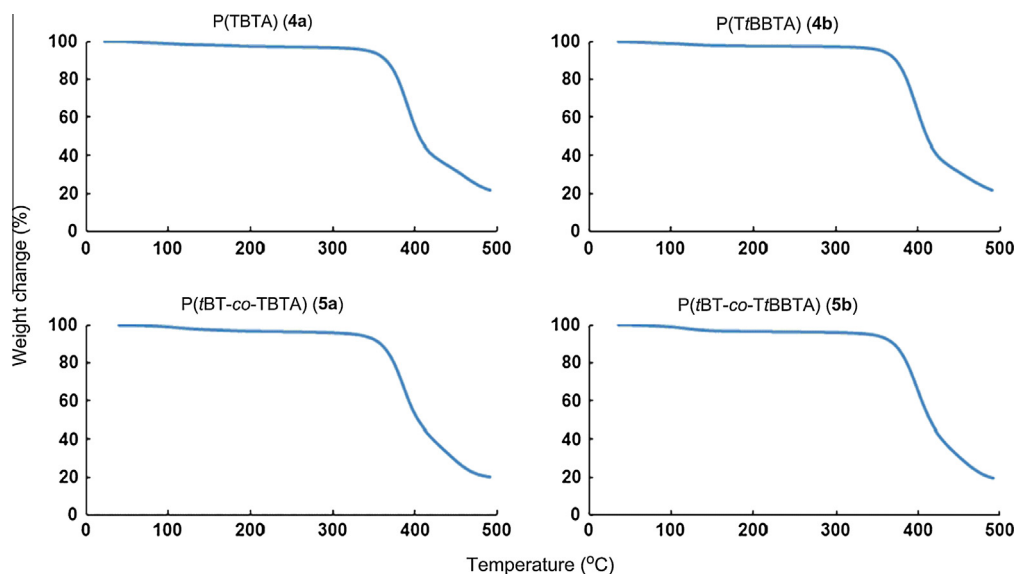
Fig. 6. TGA analysis of functionalized polymers.

Table 1
Elemental analysis of the polymer films by XPS after soaking for 24 h in (a) deionized water, (b) 0.1 M CuSO$_4$ solution.

	C (atom%)		N (atom%)		O (atom%)		Cl (atom%)		S (atom%)		Cu^{2+} (atom%)	
	a	b	a	b	a	b	a	b	a	b	a	b
PVBC	85.39	82.24	0	0	5.01	8.02	6.96	6.45	0	0	0	0
P(TBTA) (**4a**)	76.41	67.66	16.66	20.00	6.93	9.26	0	0	0	1.53	0	1.55
P(TtBBTA) (**4b**)	79.30	75.24	13.44	14.25	6.15	7.91	0	0	0	0.53	0	0.63
P(tBT-co-TBTA) (**5a**)	73.06	74.71	14.81	13.69	8.53	7.93	0	0	0	0.30	0	0.36
P(tBT-co-TtBBTA) (**5b**)	76.72	73.64	15.57	14.53	5.37	8.12	0	0	0	0.58	0	0.56
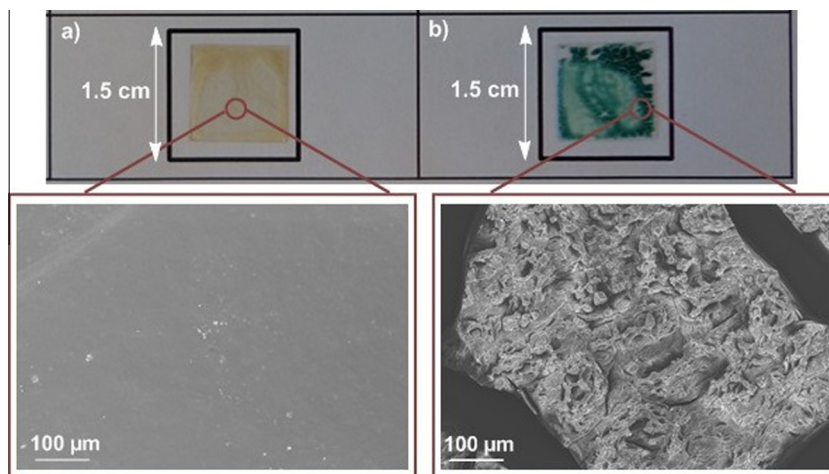
Fig. 7. Drop-casted P(TBTA) (**4a**) on glass surface soaked for 24 h in (a) deionized water, (b) 0.1 M CuSO$_4$ solution.

almost unchanged after soaking in either deionized water or the CuSO$_4$ solution. For P(TBTA) (**4a**) the final film is not totally uniform in thickness. Fig. 7 shows SEM micrographs of P(TBTA) (**4a**) films after exposure to deionized water and to 0.1 M CuSO$_4$ solution. The roughness of the film is visible to the naked eye. Nevertheless before soaking in the Cu(II) solution the film is continuous, and upon coordinating to Cu(II) ions, the film of P(TBTA) (**4a**) is restructured into discrete islands of polymeric material on the surface. Moreover, the color of the P(TBTA) (**4a**) changes from yellow to deep blue as a direct indication of copper uptake.

The polymer films of co-polymer P(tBT-co-TBTA) (**5a**) remains uniform after exposure to the copper solution; however it does not absorb copper ions as well as the homopolymer P(TBTA) (**4a**)

as monitored by XPS analysis. Unlike P(TBTA), none of the other polymers show any color change or other visible structural changes in appearance upon immersion in the CuSO$_{4s}$ solution. We speculate that this is due to the increased hydrophobicity of these films that limits the penetration of copper ions deeper into the films.

4. Conclusions

In summary, a simple one-pot method for the direct functionalization of polyvinylbenzyl chloride (PVBC) with a TBTA ligand via the CuAAC click reaction has been developed, using a method

where the final triazole ring of the ligand is created simultaneously to the attachment to the polymer backbone. Furthermore, a new *tert*-butyl substituted TBTA ligand has been synthesized and linked to PVBC. Co-polymers of these ligands and a *tert*-butyl-substituted monotriazole were also prepared. The studied polymers had glass transition in the 82–105 °C range and showed excellent thermal stability at temperatures up to 340 °C as monitored by TGA. The basic function of the polymers to absorb copper(II) ions has been demonstrated by exposing thin films of the polymers to an aqueous 0.1 M solution of $CuSO_4$ and monitoring the morphology and elemental composition by XPS.

By smart material design, the goal is to develop these polymers for the preparation of coating materials that absorbs naturally abundant Cu(II) and Cu(I) ions from seawater. Studies of the electrochemical behavior of these new polymers are in progress and will be reported in due course. The high solubility and tailored hydrophobicity of these polymers in a wide range of organic solvents is a crucial factor for their further use in various applications. We anticipate that the polymers may also find use in other applications, for instance as supports for catalysts in organic synthesis.

Acknowledgment

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.reactfunctpolym.2014.05.008.

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