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1,2,3-Triazolium-based poly(acrylate ionic liquid)s

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ABSTRACT

Nitroxide-mediated radical polymerization of a tailor-made acrylate carrying a 1,2,3-triazole group with an undecanoyl spacer affords a well-defined (M_n = 7860 g mol^{-1} and $Đ$ = 1.39) neutral polyacrylate precursor. A series of 1,2,3-triazolium-based poly(ionic liquid)s (TPILs) is then obtained by straightforward quaternization of the 1,2,3-triazole groups with methyl iodide and subsequent anion metathesis reactions. Among the prepared materials, TPIL with bis(trifluoromethane)sulfonimide anion exhibits low glass transition temperature (T_g = −40 °C), high thermal stability (T_{d10} = 325 °C) and anhydrous ionic conductivity of 4 × 10^{-6} S cm^{-1} at 30 °C, as measured by differential scanning calorimetry, thermogravimetric analysis and broadband dielectric spectroscopy, respectively.

1. Introduction

Poly(ionic liquid)s (PILs) refer to a particular class of polyelectrolytes possessing an ionic liquid (IL) moiety in the repeating unit. PILs have gathered great interest in the fields of polymer chemistry and materials science owing to unique combination of the properties from ILs (high ionic conductivity, thermal and chemical stabilities) and polymers (mechanical stability, processing and tunable macromolecular design). A constantly increasing library of PILs combining imidazolium, pyrrolidinium, pyridinium, ammonium, or phosphonium cations with counter anions such as halides (e.g. Br$^-$, I$^-$), inorganic fluorides (e.g. PF_6^-, BF_4^-) or perfluorinated sulfonimides (e.g. $(CF_3SO_2)_2N^-$, $(CF_3CF_2SO_2)_2N^-$)) has been reported so far [1–3]. Among those, imidazolium-based PILs have emerged as an archetype and demonstrated their ability to substitute liquid electrolytes in applications such as dye sensitized solar cells, fuel cells, light-emitting electrochemical cells, batteries, sensors, actuators, field effect transistors, electrochromic devices, switchable surfaces, permselective membranes, (nano)composites and catalysis [4–6]. Imidazolium-based PILs (IPILs) are classically prepared by either post-polymerization chemical modification of neutral polymers or by polymerization of an IL monomer using either step growth or chain growth polymerization techniques. The latter is preferred though when control of the polymer chain length and microstructure are desirable. Therefore, controlled radical polymerizations of imidazolium-functionalized methacrylate [7–10], methacrylamide [8,9], styrenic [11,12], *N*-vinyl-imidazolium [13–15], and acrylate [16,17] monomers have been widely investigated using atom transfer radical polymerization (ATRP) [7,11,12,16,17], reversible addition fragmentation transfer (RAFT) polymerization [8–10,14], or cobalt mediated radical polymerization (CMRP) [13,15]. To our knowledge there are no reports of the direct polymerization of IL monomers by nitroxide mediated radical polymerization (NMRP) so far. Implementation of these polymerization techniques in the synthesis of IPILs has notably opened new avenues for the design of tailor-made block copolymers comprising PIL segments [10,13,17–23], and stimuli responsive nanostructured ion conducting polymer materials with high structural order at the meso- and nanoscales [8,9,14,24].

The outstanding features of the copper-catalyzed azide-alkyne cycloaddition (CuAAC), i.e. versatility, high efficiency and robustness, have promoted the development of an extremely broad palette of polymer materials containing 1,2,3-triazole units [25–29]. Up to now, this process has been mostly used as an efficient conjugation tool but the properties of the resulting 1,2,3-triazole unit have been scarcely addressed [30–32]. We have recently proposed a straightforward synthetic route to a new class of ion conducting materials possessing 1,2,3-triazolium charged units by associating CuAAC step growth polymerization with efficient 1,2,3-triazole

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quaternization and anion metathesis methodologies [33–35]. The combination of CuAAC attributes with those of modern macromolecular engineering techniques thus paves the way to the development of a broad library of 1,2,3-triazolium-based ion conducting materials [36,37], in agreement with the strong need of the PIL community to generate highly functional materials in a simple and controlled manner. With this in mind, we extend the scope of our seminal report on 1,2,3-triazolium-based ionenes to the synthesis of low T_g ion conducting polyacrylates in this paper. Nitroxide mediated radical polymerization (NMRP) of a 1,2,3-triazole-functionalized acrylate affords a polyacrylate precursor carrying pendant 1,2,3-triazole groups which can be further derivatized into a broad range of 1,2,3-triazolium-based poly(ionic liquid)s (TPILs) by alkylation and anion metathesis reactions (Scheme 1). This strategy enables the modular preparation of a library of well-defined TPILs issued from a single poly(1,2,3-triazole) precursor. Conversely to the polymerization of different IL monomers, this approach allows establishing a precise structure–properties relationship of a series of ion conducting materials with different counter anions and quaternizing groups but identical microstructure.

2. Experimental

2.1. Materials

11-Bromoundecanol (98%), sodium azide (NaN_3, ≥99.0%), diisopropylethylamine (DIPEA, 99%), 1-pentyne (99%), iodomethane (CH_3I, 99%), copper(I) iodide triethylphosphite ($CuIP(OEt)_3$, 97%), acryloyl chloride (≥99.0%), *N-tert*-butyl-*N*-(2-methyl-1-phenylpropyl)-*O*-(1-phenylethyl)hydroxylamine (99%), silver tetrafluoroborate ($AgBF_4$, ≥99.99%), lithium hexafluorophosphate ($LiPF_6$, ≥99.99%), bis(trifluoromethane)sulfonimide lithium salt ($LiNTf_2$, 99.95%), and all solvents were purchased from Aldrich and used as received. 11-Azidoundecanol **1** was synthesized as described earlier [38].

2.2. Characterizations

^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Bruker DRX300 spectrometer in $CDCl_3$ or DMSO-d_6. Peak multiplicities are designated by m = multiplet, s = singlet, d = doublet, t = triplet, br = broad and coupling constants, designated by *J*, are given in Hz for doublets and triplets. Differential scanning calorimetry (DSC) measurements were performed on a DSC Q200 apparatus (TA Instruments) by applying two cycles in the temperature range of −80 to 120 °C at the heating rate of 10 °C min^{-1} under helium atmosphere. T_g values were measured during the second heating. Thermogravimetric analysis (TGA) was performed under helium using a TGA Q500 apparatus (TA Instruments) at a heating rate of 10 °C min^{-1}. Size exclusion chromatography (SEC) was carried out at 22 °C on a setup comprising a Shimadsu LC 20AD pump, a Perkin Elmer Series 200 automatic injector, a Wyatt TREOS 3 angles Light scattering detector, a Shimadzu RID 10A Refractometer, and a PL gel 5 μm Mixed C (300 × 7.5 mm, polystyrene/divinylbenzene) column using chloroform as the eluant. A 2 mg mL^{-1} solution was prepared in chloroform and filtered through a 0.45 μm pore size PTFE filter prior to the measurements. Number average molar masses (M_n), weight average molar masses (M_w) and molar mass distributions ($D = M_w/M_n$) were calculated using a refractive index calibration curve obtained from polystyrene standards. ASTRA 6 software was utilized for the treatment of the results. The ionic conductivity was measured using a high resolution Alpha-Analyzer (Novocontrol GmbH) assisted by a Quatro temperature controller. The sample was prepared by casting a solution of the polymer in acetone on a freshly polished platinum electrode followed by an overnight annealing treatment at 120 °C under vacuum. The polymer film was then pressed against another platinum electrode and the thickness was controlled by employing 20 μm thick Teflon spacers. The prepared measurement cell was annealed for 4 h at 120 °C under a pure nitrogen atmosphere. Frequency sweeps were performed isothermally from 10 MHz to 0.1 Hz by applying a sinusoidal voltage of 0.1 V over a range of temperature varying from 120 to −60 °C. The temperature was controlled by heating the sample under a flow of pure nitrogen, which excludes the presence of oxygen and humidity in the measurement chamber. The thermal stability was set to be better than 0.1 K in absolute values with relative variations less than 0.2 K min^{-1}.

2.3. Synthetic procedures

2.3.1. Synthesis of **2**

A solution of **1** (10.0 g, 46.9 mmol), 1-pentyne (3.83 g, 56.4 mmol), $CuIP(OEt)_3$ (0.839 g, 2.35 mmol) and diisopropylethylamine (6.06 g, 46.9 mmol) in tetrahydrofuran (150 mL) was stirred at room temperature for 4 days. The volatiles were evaporated and the crude product was purified by flash chromatography using a 1:1 mixture of petroleum ether and ethyl acetate. The solvents were evaporated and 1,2,3-triazole-functionalized undecanol **2** was recovered as a white powder (6.50 g, 47.0%). ^1H NMR (300 MHz, $CHCl_3$, δ, ppm): 7.23 (s, $NC{=}C\mathbf{H}N$), 4.26 (t, 2H, $J = 7.2$ Hz, $CH_2C\mathbf{H}_2N$), 3.60 (t, 2H, $J = 6.6$ Hz, $C\mathbf{H}_2OH$), 2.62 (t, 2H, $J = 7.5$ Hz, $CH_3CH_2C\mathbf{H}_2C{=}CH$), 2.09 (s, 1H, $CH_2O\mathbf{H}$), 1.84 (t, 2H, $J = 6.9$ Hz, $C\mathbf{H}_2CH_2N$), 1.64 (m, 2H, $CH_3C\mathbf{H}_2CH_2C{=}CH$), 1.50 (m, 2H, $C\mathbf{H}_2CH_2OH$), 1.22 (br, 14H, $CH_2CH_2(C\mathbf{H}_2)_7CH_2CH_2$), 0.92 (t, 3H, $J = 7.3$ Hz, $C\mathbf{H}_3CH_2CH_2C{=}CH$). ^{13}C NMR (75 MHz, $CHCl_3$, δ, ppm): 148.05 ($N\mathbf{C}{=}CHN$), 120.38 ($NC{=}\mathbf{C}HN$), 62.71 ($\mathbf{C}H_2OH$), 50.05 ($\mathbf{C}H_2N$), 32.67 ($\mathbf{C}H_2CH_2OH$), 30.20 ($\mathbf{C}H_2CH_2N$), 29.36, 29.26, 29.23, 29.18, 28.80, 26.32, 25.63 ($NCH_2CH_2(\mathbf{C}H_2)_7CH_2CH_2OH$), 27.56 ($CH_3CH_2\mathbf{C}H_2C{=}CH$), 22.61 ($CH_3\mathbf{C}H_2CH_2C{=}CH$), 13.67 ($\mathbf{C}H_3CH_2CH_2C{=}CH$). HRMS (*m/z*): calculated for $C_{16}H_{32}N_3O$, 282.2540; found 282.2545 $[M + H]^+$.

2.3.2. Synthesis of **3**

A solution of **2** (4.00 g, 14.2 mmol), hydroquinone (0.10 g, 0.91 mmol) and triethylamine (7.19 g, 71.2 mmol) in dichloromethane (50 mL) was stirred at 0 °C under argon. Acryloyl chloride (1.92 g, 21.4 mmol) was added drop-wise and the reaction mixture was kept stirring under argon overnight at room temperature. The reaction mixture was filtered, the volatiles were evaporated and the crude product was purified by flash chromatography using a 85:15 mixture of petroleum ether and ethyl acetate. The solvents were evaporated to obtain 1,2,3-triazole-functionalized undecanoyl acrylate **3** as a white powder (1.65 g, 27.9%). ^1H NMR (300 MHz, $CHCl_3$, δ, ppm): 7.23 (s, 1H, $NC{=}C\mathbf{H}N$), 6.37 (dd, 1H, $J_1 = 17.4$ Hz, $J_2 = 1.5$ Hz, $C\mathbf{H}_{cis}H_{trans}{=}CH$), 6.09 (dd, 1H, $J_1 = 17.4$ Hz, $J_2 = 10.2$ Hz, $CH_2{=}C\mathbf{H}$), 5.79 (dd, 1H, $J_1 = 10.2$ Hz, $J_2 = 1.5$ Hz, $CH_{cis}\mathbf{H}_{trans} = CH$), 4.28 (t, 2H, $J = 7.2$ Hz, $CH_2C\mathbf{H}_2N$), 4.12 (t, 2H, $J = 6.9$ Hz, $CH_2C\mathbf{H}_2O$), 2.67 (t, 2H, $J = 7.2$ Hz, $CH_3CH_2C\mathbf{H}_2C{=}CH$), 1.85 (m, 2H, $C\mathbf{H}_2CH_2N$), 1.66 (m, 4H, $CH_3C\mathbf{H}_2CH_2C{=}CH$ and $C\mathbf{H}_2CH_2O$), 1.39–1.17 (br, 14H, $NCH_2CH_2(C\mathbf{H}_2)_7CH_2CH_2O$), 0.94 (t, 3H, $J = 7.2$ Hz, $C\mathbf{H}_3CH_2CH_2C{=}CH$). ^{13}C NMR (75 MHz, $CHCl_3$, δ, ppm): 166.27 ($\mathbf{C}{=}O$), 148.09 ($N\mathbf{C}{=}CHN$), 130.38 ($\mathbf{C}H_2{=}CH$), 128.56 ($CH_2{=}\mathbf{C}H$), 120.33 ($NC{=}\mathbf{C}HN$), 64.60 ($\mathbf{C}H_2O$), 50.07 ($\mathbf{C}H_2N$), 30.28 ($\mathbf{C}H_2CH_2N$), 29.34, 29.12, 28.91, 26.42, 25.82 ($NCH_2CH_2(\mathbf{C}H_2)_7CH_2O$), 28.51 ($\mathbf{C}H_2CH_2O$), 27.64 ($CH_3CH_2\mathbf{C}H_2C{=}CH$), 22.68 ($CH_3\mathbf{C}H_2CH_2C{=}CH$), 13.72 ($\mathbf{C}H_3CH_2CH_2C{=}CH$). HRMS (*m/z*): calculated for $C_{19}H_{34}N_3O_2$, 336.2646; found 336.2640 $[M + H]^+$.

2.3.3. General procedure for nitroxide mediated radical polymerization, synthesis of **5**

A solution of **3** (330 mg, 0.98 mmol) and *N-tert*-butyl-*N*-(2-methyl-1-phenylpropyl)-*O*-(1-phenylethyl)hydroxylamine **4** (1.3 mg, 3.9×10^{-3} mmol) in dimethylformamide (2 mL) was sealed under

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