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COMMUNICATION

Poly(vinyl ester 1,2,3-triazolium)s: a New Member of the Poly(Ionic Liquid)s Family

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A vinyl ester monomer carrying a pendant 1,2,3-triazole group is synthesized in two steps and polymerized by cobalt-mediated radical polymerization. Subsequent alkylation with *N*-methyl bis[(trifluoromethyl)sulfonyl]imide affords the corresponding poly(vinyl ester 1,2,3-triazolium). This unprecedented example of poly(vinyl ester ionic liquid) exhibits an ionic conductivity of 9.2×10^{-7} S/cm at 30 °C.

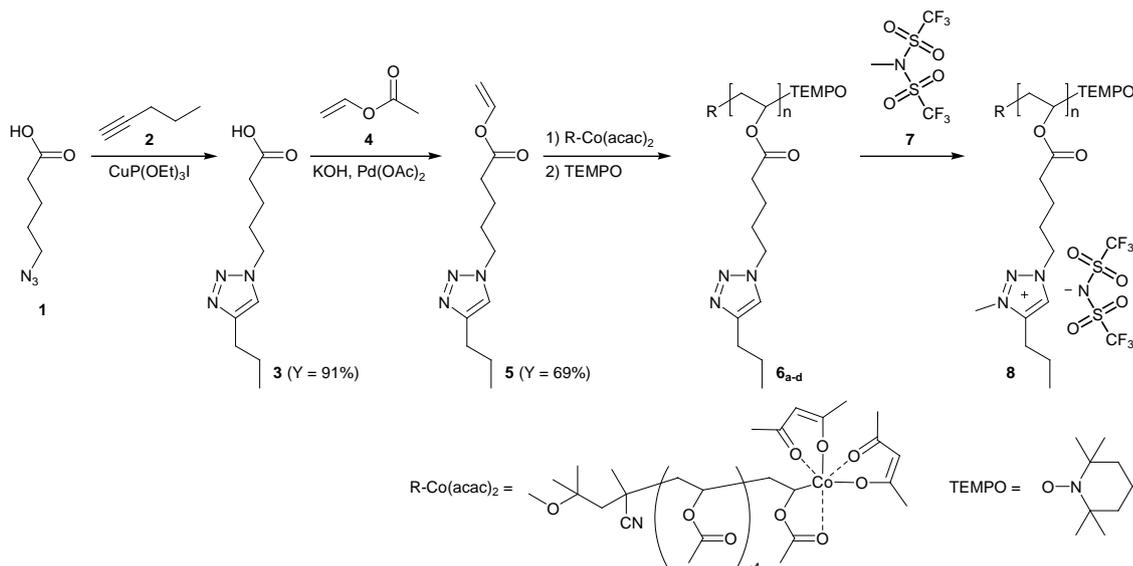
Poly(ionic liquid)s (PILs) are a special class of polyelectrolytes that gather increasing interest in fields such as dye sensitized solar cells, fuel cells, light-emitting electrochemical cells, batteries, sensors, actuators, field effect transistors, electrochromic devices, switchable surfaces, permselective membranes, (nano)composites and catalysis.¹ They combine the unique properties of ILs (high ionic conductivity, thermal and chemical stabilities) with those of polymers (mechanical stability, processing and tunable macromolecular design). Their broad structural variety relies on the numerous combinations of ammonium, pyridinium, pyrrolidinium, imidazolium, phosphonium or 1,2,3-triazolium cations with counter anions such as halides (e.g. Cl⁻, Br⁻, I⁻), fluorides (e.g. PF₆⁻, BF₄⁻), perfluorinated sulfonimides (e.g. (CF₃SO₂)₂N⁻) or N(CN)₂⁻ as well as a wide range of polymer microstructures.² The synthesis of PILs has been applied to most polymer classes including for instance poly(styrene)s, poly((meth)acrylate)s, poly(*N*-vinyl-imidazolium)s, poly(vinyl ether)s, polyesters, polyurethanes, poly(norbornadiene)s or polyolefins.^{1,2}

We have recently pioneered the synthesis of 1,2,3-triazolium-based PILs (TPILs).³ Their synthesis through copper-catalyzed azide-alkyne cycloaddition (CuAAC) offers unprecedented opportunities for PILs macromolecular design. By merging CuAAC and step growth or chain growth polymerization techniques together with efficient 1,2,3-triazole quaternization and anion metathesis methodologies, several classes of 1,2,3-triazolium analogues of previously reported PILs have been synthesized, i.e. poly(acrylate)s, poly(styrene)s and ionenes.³ Besides, Nulwala and co-workers have developed poly(4-vinyl-1,2,3-triazolium)s, while Schlaad and co-workers have reported on polypeptoids carrying pendant 1,2,3-

triazolium groups.⁴ The combination of the CuAAC attributes with modern macromolecular engineering is thus able to further extend the existing library of PILs and to increase their multifunctional nature.⁵ Herein we demonstrate the synthesis of a new class of PILs belonging to the poly(vinyl ester) family that do not have any structural analogue in the current library of PILs with classical cations. The applicative performances of PILs being strongly structure-dependent, it is both fundamentally and industrially relevant to develop new PILs with enhanced properties.

1,2,3-Triazole-functionalized vinyl ester monomer **5** was synthesized in two steps (**Scheme 1**). First, CuAAC between 4-azidovaleic acid **1** and 1-pentyne **2** yielded 1,2,3-triazole-functionalized carboxylic acid **3** in 91% yield. The high purity of **3** was confirmed by ¹H and ¹³C NMR spectroscopy (**Fig. S1 and S2, ESI†**) as well as ESI-HRMS. Monomer **5** was then obtained in 69% yield by palladium-catalyzed vinyl exchange between **3** and vinyl acetate **4**,⁶ while the starting carboxylic acid **3** could be recovered quantitatively. The purity of **5** was again demonstrated by ¹H and ¹³C NMR spectroscopy (**Fig. S3 and S4, ESI†**) and ESI-HRMS.

The cobalt-mediated radical polymerization (CMRP) technique was selected for the polymerization of **5** due to its high efficiency in controlling the radical polymerization of non-conjugated vinyl monomers such as vinyl esters under mild experimental conditions.⁷ Polymerization of **5** was carried out at 30 °C in dimethylsulfoxide (DMSO) using an alkyl-cobalt(III) as both the initiator and the controlling agent.^{7a} Under these conditions, the SEC chromatograms are monomodal although a slight tailing is observed at the low molar mass side of the peaks (**Fig. 1**). The polymer molar mass increases from 4700 to 7200 g/mol while monomer conversion increases from 38 to 80%, and relatively low *D* values increasing from 1.10 to 1.22 are obtained (**Table S1, ESI†**). The number average molar mass of **6a** obtained by integration of the chain end signal at 3.07 ppm (for the methyl protons of the initiator chain end) and the polymer signals (7.79, 4.73 or 4.26 ppm) is in good agreement with the value obtained from SEC using PS calibration, i.e. 7.3 and 7.2 kDa, respectively.



Scheme 1. Synthesis of ion conducting poly(vinyl ester 1,2,3-triazolium) **8**.

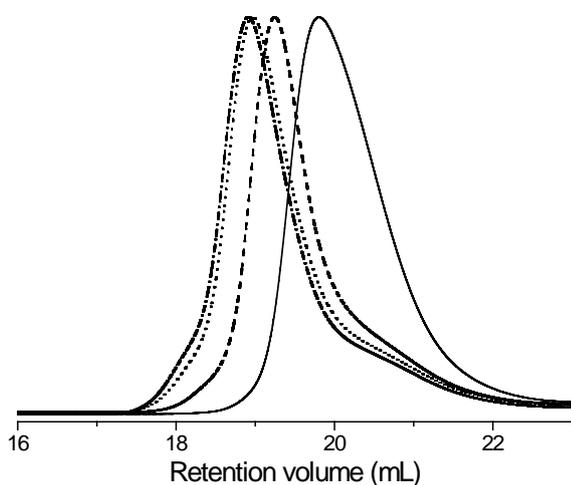


Fig. 1 Evolution of SEC traces for the cobalt-mediated radical polymerization of **5** at 30 °C in dimethyl sulfoxide (See Table S1, ESI† for polymerization conditions).

1,2,3-Triazole groups of polymer **6_d** were then alkylated quantitatively in *N,N*-dimethylformamide using *N*-methyl bis(trifluoromethyl)sulfonyl-imide **7** to afford the corresponding poly(vinyl ester 1,2,3-triazolium) **8**. It has been previously demonstrated that **7** is an efficient quaternizing agent able to readily afford pyridinium, imidazolium or 1,2,3-triazolium cations with bis[(trifluoromethyl)sulfonyl]imide (TFSI) counter anion without the requirement for an anion exchange procedure.⁸ This anion generally provides PILs with higher ionic conductivity compared to PILs having other typical counter anions.²

Assignments of ¹H NMR signals from **6_d** and **8** (**Fig. 2**) confirm the success of both the polymerization and the quaternization processes. Except protons signals from the polymer backbone, all signals are impacted by quaternization of the 1,2,3-triazole groups. However, the most significant changes correspond to the down-field shifting of the *N*-1 and *C*-4 methylene signals (from 4.26 to 4.52 ppm and from 2.52 to 2.80 ppm, respectively), the disappearance of the 1,2,3-triazole proton at 7.79 ppm as well as the quantitative appearance of the 1,2,3-triazolium proton at 8.67 ppm together with the *N*-3 methyl group at 4.16 ppm with a 1:3 ratio of integrals.

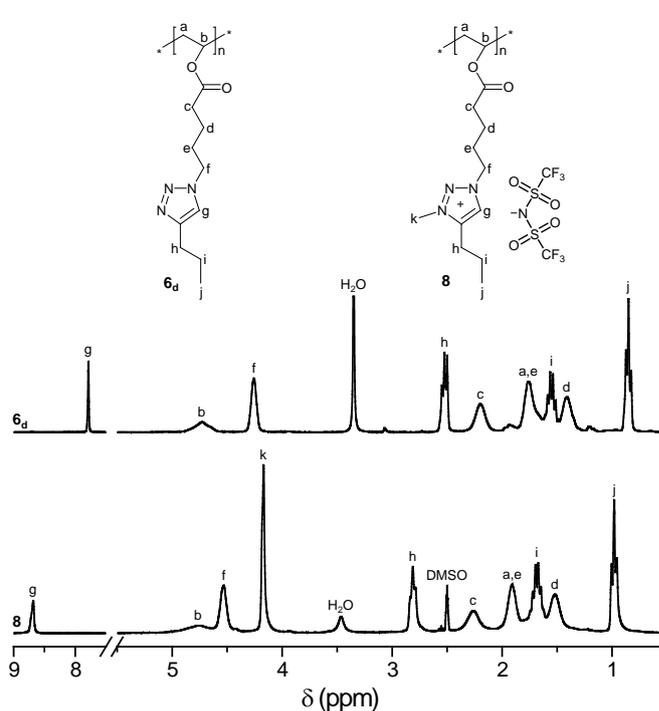


Fig. 2 ¹H NMR (DMSO-*d*₆) of poly(vinyl ester 1,2,3-triazole) **6_d** and poly(vinyl ester 1,2,3-triazolium) **8**.

Poly(vinyl ester 1,2,3-triazolium) **8** presents a low dispersity (*D* = 1.19; Table 1), very similar to the neutral precursor **6_d**, and its SEC chromatogram (obtained using a 10mM solution of LiTFSI in THF as eluent) remains monomodal (**Figure S5**, ESI†).⁹ Quaternization of the 1,2,3-triazole group modified the solubility of TPIL **8** compared to **6_d** (**Table S2**, ESI†). Both polymers are soluble in acetone, acetonitrile (CH₃CN), DMF and DMSO, while insoluble in water (H₂O), heptane and diethyl ether (Et₂O). However, after the quaternization process a decrease in solubility is observed in methanol (MeOH), ethyl acetate (EtOAc), dichloromethane (CH₂Cl₂), chloroform (CHCl₃), toluene (PhCH₃) and tetrahydrofuran (THF).

Table 1. Physical properties of poly(vinyl ester 1,2,3-triazole) **6a** and poly(vinyl ester 1,2,3-triazolium) **8**.

N°	T_g (°C) ^a	T_{d10} (°C) ^b	$M_{n,SEC}$ (kDa)	\bar{D}	σ_{DC} at 30 °C (S/cm) ^f
6a ^c	-25	307	7.2 ^d	1.21 ^d	-
8	-16	304	8.8 ^e	1.19 ^e	9.2×10^{-7}

Values obtained by ^a) DSC; ^b) TGA; ^c) ¹H NMR; ^d) SEC in THF; ^e) SEC in THF/LiTFSI; ^f) BDS.

Thermal properties were also affected upon the transformation of neutral poly(vinyl ester 1,2,3-triazole) **6a** into ion conducting poly(vinyl ester 1,2,3-triazolium) **8** (Table 1). First, a 9 °C increase in the glass transition temperature (T_g) was observed after quaternization of the 1,2,3-triazole groups. This can be explained by the significant increase in the size of the pendant substituents, and therefore the reduced mobility of the polymer chains, after introduction of the methyl group and the TFSI counter anion. The T_g of **8** is slightly higher than the values obtained for other TPILs which range from -40 to -28 °C for poly(acrylate)s and from -68 to -35 °C for ionenes containing *N*-3 methyl groups and TFSI counter anions.^{3,8b} Besides, thermal stability of **8** is relatively high and comparable to that of its neutral precursor **6a**, i.e. the temperatures at 10wt% loss (T_{d10}) are 304 and 307 °C, respectively (Fig. S6, ESI†). The temperature dependence of the anhydrous ionic conductivity of TPIL **8** was then investigated by broadband dielectric spectroscopy (BDS). The dielectric measurements, carried out after a thermal treatment for several hours at 110 °C, were performed under anhydrous conditions (flow of pure nitrogen) in a parallel plate geometry using two platinum electrodes. The complex conductivity function $\sigma^*(\omega, T)$ was measured in the broad frequency range (10^1 - 10^7 Hz) under isothermal conditions with temperatures ranging from 110 °C to -70 °C (Fig. S7, ESI†). Direct current conductivity (σ_{DC}) was derived from the plateau-value observed in the spectral dependence of the conductivity function ($\sigma' = \omega \varepsilon'' \varepsilon_0$, where ω is the frequency, ε_0 the vacuum permittivity and ε'' the dielectric loss). As generally observed, the plateau value in $\sigma^*(\omega, T)$ associated to σ_{DC} decreases and becomes shifted to lower frequencies with decreasing temperature. At temperatures near T_g (at -10 °C for **8**) the plateau disappears from the frequency window of our experiment. This is due to the significant loss in mobility of the polymeric ionic charge carriers upon vitrification of the system when approaching T_g . The evolution of the σ_{DC} values with temperature (Fig. 3) follows a typical Vogel-Fulcher-Tammann (VFT) dependence due to the correlation between the charge transport of the ionic species and the molecular mobility of the polymer matrix.¹⁰ They were thus fitted with the VFT equation (1),

$$\sigma_{DC} = \sigma_{\infty} \times \exp(-B/(T-T_0)) \quad (1)$$

where σ_{∞} is the ionic conductivity in the limit of high temperatures, B is the fitting parameter related to the activation energy of ionic conduction and T_0 is the Vogel temperature. The values obtained from the best fitting of the experimental curve are in good accordance with those previously reported for other TPILs (Table 1).^{3,8b}

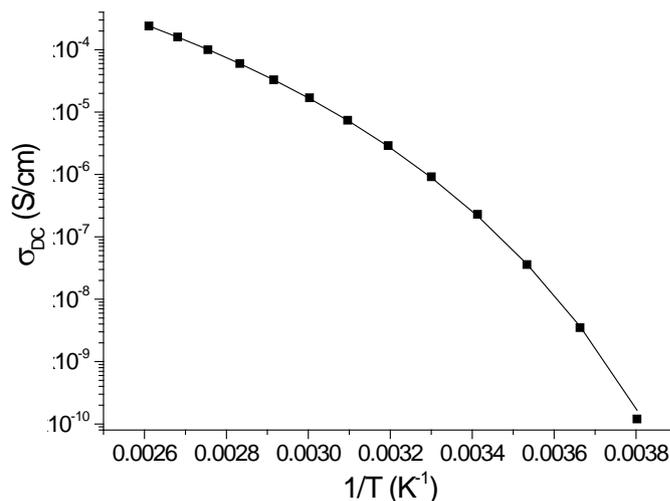


Fig. 3 Direct current conductivity (σ_{DC}) versus inverse temperature for poly(vinyl ester 1,2,3-triazolium) **8**. The solid line represents the best VFT fit of experimental data using equation 1 with $\sigma_{\infty} = 0.23$ S/cm, $B = 1220$ K and $T_0 = 205$ K.

Ionic conductivity of **8** ($\sigma_{DC} = 9.2 \times 10^{-7}$ S/cm at 30 °C) is lower than the values attained by TPIL polyacrylates and ionenes with identical *N*-3 methyl groups and TFSI counter anions which range from 4.0×10^{-6} to 2.0×10^{-5} S/cm at 30 °C. This is mainly due to the higher T_g value of **8** but ionic conductivity of poly(vinyl ester 1,2,3-triazolium)s could be optimized by varying the chemical nature and length of the *C*-4 alkyl substituents as well as the *N*-1 spacer between the polymer backbone and the 1,2,3-triazolium group. Finally, the correlation between T_g and T_0 is very good since the experimental value of $T_g - T_0$ is very close to the theoretical one, i.e. 52 and 50 °C, respectively.

Conclusions

A first example of well-defined poly(vinyl ester 1,2,3-triazolium) with bis[(trifluoromethyl)sulfonyl]imide counter anion has been synthesized by combining CuAAC, CMRP and efficient one-step quaternization. This thermally-stable polymer electrolyte has a T_g of -16 °C and an ionic conductivity of 9.2×10^{-7} S/cm at 30 °C. The developed CuAAC-based synthetic strategy offers unprecedented opportunities to finely tune the structure and properties of poly(vinyl ester 1,2,3-triazolium)s and to keep on broadening the PILs family as well. This work is currently being investigated in our research groups.

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Notes and references

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