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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 $9.2 \times 10^{-7}$ S/cm at 30 °C.
1,2,3-Triazole groups of polymer 6d 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 6d 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.

Poly(vinyl ester 1,2,3-triazolium) 8 presents a low dispersity ($D = 1.19$; Table 1), very similar to the neutral precursor 6a, 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 6a (Table S2, ESI†). Both polymers are soluble in acetone, acetonitrile (CH$_3$CN), DMF and DMSO, while insoluble in water (H$_2$O), heptane and diethyl ether (Et$_2$O). However, after the quaternization process a decrease in solubility is observed in methanol (MeOH), ethyl acetate (EtOAc), dichloromethane (CH$_2$Cl$_2$), chloroform (CHCl$_3$), toluene (PhCH$_3$) and tetrahydrofuran (THF).
treatment for several hours at 110 °C, were performed under (BDS). The dielectric measurements, carried out after a thermal function
TPIL
The temperature dependence of the anhydrous ionic conductivity of anions.3,8b Besides, thermal stability of
for ionenes containing anions.3,8b Thermal
TPIL
values of
To
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 (Tg) are 304 and 307 °C, respectively (Fig. S6, ESI†). The temperature dependence of the anhydronic 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 anhydronic conditions (flow of pure nitrogen) in a parallel plate geometry using two platinum electrodes. The complex conductivity function σ*(ω,T) was measured in the broad frequency range (10–103 Hz) under isothermal conditions with temperatures ranging from 110 °C to –70 °C (Fig. S7, ESI†). Direct current conductivity (σDC) was derived from the plateau-value observed in the spectral dependence of the conductivity function (σ = 6εωε0ω0, where ω is the frequency, ε0 the vacuum permittivity and ε the dielectric loss). As generally observed, the plateau value in σ*(ω,T) associated to σDC decreases and becomes shifted to lower frequencies with decreasing temperature. At temperatures near Tg (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 Tg.

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 (Tg) 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 Tg

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

<table>
<thead>
<tr>
<th>N°</th>
<th>Tg (°C)</th>
<th>Td0 (°C)</th>
<th>Mz,SEC (kDa)</th>
<th>D</th>
<th>σDC at 30 °C (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>-25</td>
<td>307</td>
<td>7.2</td>
<td>1.21</td>
<td>9.2 × 10^-7</td>
</tr>
<tr>
<td>8</td>
<td>-16</td>
<td>304</td>
<td>8.8</td>
<td>1.19</td>
<td>9.2 × 10^-7</td>
</tr>
</tbody>
</table>

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

Ionic conductivity of 8 (σDC = 9.2 × 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 Tg value of 8 but ionic conductivity of poly(vinyl ester 1,2,3-triazolium) 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 Tg and To is very good since the experimental value of Tg – To 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]sulfonylimide counter anion has been synthesized by combining CuAAC, CMRP and efficient one-step quaternization. This thermally-stable polymer electrolyte has a Tg of –16 °C and an ionic conductivity of 9.2 × 10^-2 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) and to keep on broadening the PILs family as well. This work is currently being investigated in our research groups.

Acknowledgment
E.D. gratefully acknowledges the financial support from the Institut Universitaire de France (IUF). A.D. and C.D. thanks BELSPO (IUA5 P7/05 – Functional Supramolecular Systems) for financial support. A.D. and C.D. are Research Associate and Director of the F.R.S.-FNRS, respectively. Gregory Cartigny and Robin Skibinski are gratefully acknowledged for their technical assistance.

Notes and references

De acknowledges the financial support from the Institut Universitaire de France (IUF). A.D. and C.D. thanks BELSPO (IUA5 P7/05 – Functional Supramolecular Systems) for financial support. A.D. and C.D. are Research Associate and Director of the F.R.S.-FNRS, respectively. Gregory Cartigny and Robin Skibinski are gratefully acknowledged for their technical assistance.

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Electronic Supplementary Information (ESI) available: Synthetic and characterization details. See DOI: 10.1039/c000000x/


