

Short Note

1-Octyl-3-(3-(1-methylpyrrolidiniumyl)propyl)imidazolium Bis(trifluoromethane)sulfonimide

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Received: 7 October 2019; Accepted: 18 November 2019; Published: 19 November 2019

Abstract: The title compound 1-octyl-3-(3-(1-methylpyrrolidiniumyl)propyl)imidazolium bis(trifluoromethane)sulfonimide was prepared in three steps. This asymmetrical dicationic ionic liquid (ADIL) is composed of two different positively charged head groups (1-octylimidazolium and methylpyrrolidinium cations), which are linked through a propyl alkyl chain and by two bis(trifluoromethane)sulfonimide anions. The final ADIL was obtained by a simple metathesis reaction of the corresponding dibromide ionic liquid, in turn prepared by alkylation of 3-(3-bromopropyl)-1-propylimidazolium bromide. The ADIL structure and those of its precursors were confirmed through NMR and infrared spectroscopy, and the thermal properties of all compounds were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Density, solubility, and viscosity were measured for the prepared compounds.

Keywords: ionic liquids (ILs), dicationic ionic liquids (DILs), asymmetrical dicationic ionic liquids (ADILs)

1. Introduction

Ionic liquids (ILs) are organic salts, liquid at room temperature or below 100 °C, composed by an organic cation (e.g., imidazolium, ammonium, or phosphonium) and an organic or an inorganic anion [1]. Due to their unique physicochemical properties [2], including negligible vapor pressure under ambient conditions, low flammability, high ionic, and thermal conductivity [3,4]; high refractive index [5]; wide electrochemical potential window; excellent thermal, chemical, and radiochemical stability [6]; as well as remarkable solvent capability, in the last two decades, ILs have attracted enormous interest. ILs are considered designer solvents due to the fact that, through modifications of the cation and/or of the anion portion, their physicochemical properties can easily be fine-tuned. For this reason, ILs are used in various fields spanning from solvents [7] or catalysts [8,9] for organic reactions, to electrochemistry [10,11], from biopolymer dissolution [12,13] and modification [14], to their use as surfactant and dispersing agents [15,16].

Dicationic (or geminal) ionic liquids (DILs) belong to a very interesting subclass of ILs. Typically, they are composed by two cations connected by an alkyl or polyether [17] linker. DILs may present further external alkyl chains on the cation part and are characterized by two counteranions, which can be of the same kind or different kinds. Because of these features, dicationic ILs (DILs) have been shown to possess superior tunability potential when compared to monocationic ILs, and this advantage has been exploited for designing DILs for specific applications; for example, DILs exhibited much higher thermal degradation temperatures [18,19], wider liquid ranges, higher densities, higher glass transition temperatures and melting points, larger surface tensions, higher shear viscosities [20], and electrochemical windows in the range of 4.3 V to 4.7 V

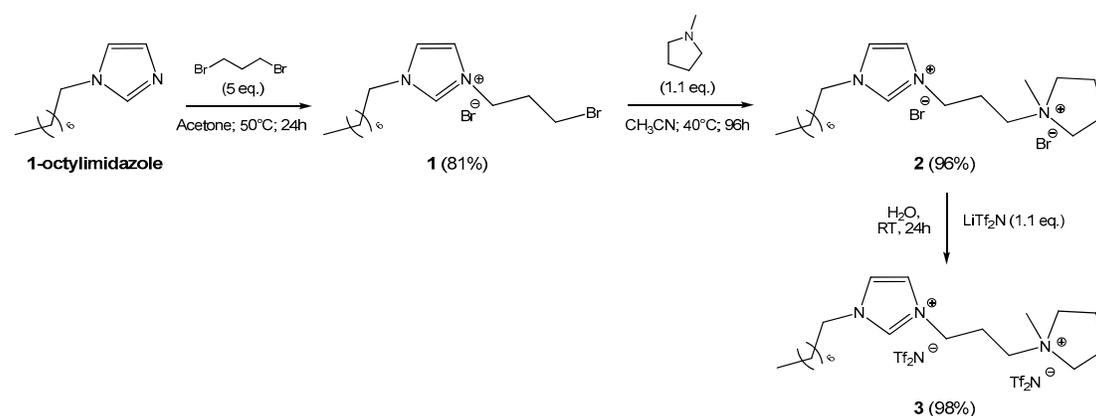
[21]. These properties offer a wider portfolio of possible applications, such as their use as stationary phases for gas chromatography capillary columns [22], high temperature lubricants, and solvents and catalysts in high-temperature reactions [23–26]. Besides, the electrochemical properties make them attractive as electrolytes in high-temperature batteries [27,28] and in dye-sensitized solar cells [29].

In recent years, asymmetrical dicationic ionic liquids (ADILs), that is, DILs with different cationic head groups, have been studied and compared to traditional DILs. According to the collected results, they provide a greater degree of flexibility and hence more options for the fine-tuning of their physico-chemical properties.

In this context, we describe the synthesis of a new ADIL characterized by both a pyrrolidinium and an imidazolium cation. The two different positively charged moieties, bearing a methyl and octyl alkyl chain, respectively, were linked through a propyl alkyl chain. The target ADIL and all the intermediates were characterized by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and FTIR. Finally, solubility, density, and viscosity at 25 °C were measured, and the thermal properties of all prepared compounds were analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to evaluate the operating range of these new set of ILs.

2. Results and Discussion

Herein, we report a synthetic procedure for the synthesis of 1-octyl-3-(3-(1-methylpyrrolidiniumyl)propyl)imidazolium bis(trifluoromethane)sulfonimide, $\text{C}_3(\text{C}_8\text{Im})(\text{C}_1\text{Pyr})/2 \text{ Tf}_2\text{N}$ (**3**). ADIL **3** was synthesized in three steps, as shown in Scheme 1.



Scheme 1. Synthetic procedure for synthesis of 1-octyl-3-(3-(1-methylpyrrolidiniumyl)propyl)imidazolium bis(trifluoromethane)sulfonimide, $\text{C}_3(\text{C}_8\text{Im})(\text{C}_1\text{Pyr})/2 \text{ Tf}_2\text{N}$.

In the first step, the synthesis of 3-(3-bromopropyl)-1-octylimidazolium bromide (**1**) was performed by following the procedure reported by Zhiwen et al. [30]. 1-Octylimidazole was reacted with 1,3-dibromopropane in dry acetone at 50 °C for 24 h. The dibromide alkylating agent was used in large excess (five equivalents) to minimize the formation of the symmetric DIL byproduct. At the end of the reaction, the crude mixture was washed with diethyl ether and then purified by flash chromatography on silica gel eluted with dichloromethane/methanol (9:1, v/v) to obtain IL **1** in an 81% yield.

In the second step, *N*-methylpyrrolidine was used as the nucleophile to conduct the Menshutkin reaction on **1** in dry acetonitrile at 40 °C for 96 h. The product was washed with diethyl ether to remove the pyrrolidine excess, and bromide ADIL **2** was obtained in a high yield (96%). In the final step, the metathesis reaction was carried out on compound **2** by using lithium bis(trifluoromethane)sulfonimide (LiTf_2N) to access the bis(trifluoromethane)sulfonimide ADIL **3**. The switch from hydrophilic to hydrophobic character, via the transformation of the bromide into the Tf_2N salt, allowed for an easy recovery of the target ADIL. Indeed, ADIL **2** was soluble in water,

whereas ADIL **3** was not and was obtained after adding dichloromethane to the reaction mixture. The organic phase was washed several times with deionized water. The extent of the anion exchange and the removal of the halide anion were assessed by means of the silver nitrate test. The yield of this final anion exchange reaction was 98%. Therefore, ADIL **3** was synthesized in an overall 76% yield from 1-octylimidazole.

¹H-NMR, ¹³C-NMR, and FTIR experiments confirmed the structures and the purities of compounds **1**, **2**, and **3**. In particular, the presence of bis(trifluoromethane)sulfonimide anions in compound **3** was confirmed by the presence of a diagnostic quadruplet signal of CF₃ in the ¹³C-NMR spectrum (125.0, 121.8, 118.6, and 115.4 ppm) and the well-known bands at 1347, 1178, and 1051 cm⁻¹ in the FTIR spectrum. The density of prepared compounds and solubility in different solvents was evaluated (Table 1). With the exception of **3** in water, (AD)ILs **1–3** are soluble in all polar solvents tested.

Table 1. Density and solubility of (AD)ILs in different solvents at 25 °C.

ILs	Water	Methanol	Hexane	Acetonitrile	Dichloromethane	Density (g/cm ³)
C₃Br(C₈Im)/Br	X	X	-	X	X	1.07
C₃(C₈Im)(C₁Pyrr)/2 Br	X	X	-	X	-	1.10
C₃(C₈Im)(C₁Pyrr)/2 Tf₂N	-	X	-	X	X	1.47

The viscosities of compounds **1** and **3**, which are liquid at room temperature, were measured at different shear rates. Neither compound behaves as a Newtonian fluid (please refer to the supporting information file), and selected viscosity values at different shear rates (1.12, 12.5, and 99.9 1/s) are reported in Table 2.

Table 2. Viscosity (mPa s) of C₃Br(C₈Im)/Br (**1**) and C₃(C₈Im)(C₁Pyrr)/2 Tf₂N (**3**) at different shear rates (1/s) at 25 °C.

IL	Shear Rate (1/s)	Viscosity (mPa s)
C₃Br(C₈Im)/Br	1.12	11197
	12.5	9599.8
	99.9	3597.9
C₃(C₈Im)(C₁Pyrr)/2 Tf₂N	1.12	1133.7
	12.5	932.47
	99.9	811.14

The thermal behavior of these ADILs and of related ILs was investigated through thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermal stability was carried out by TGA (Q500 TA instruments) heating from 40 to 700 °C with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. The T_{start} 5%, T_{onset}, and T_{peak} temperatures obtained from the thermographs of the synthesized compounds (Supporting Information) are reported in Table 3. As a general trend, and in line with previous findings [31], the thermal stability increased in the following order, **1** < **2** < **3**. Note that bromide ADIL **2** displayed a thermal stability comparable to that of the symmetric DIL (C₃(C₈Im)₂/2 Br [31]). Conversely, ADIL **3** resulted less stable (~50 °C) than the corresponding symmetric DIL (C₃(C₈Im)₂/2 Tf₂N [31]). Therefore, it seems that the effect of the cationic structural variations is appreciable only with the less nucleophilic anion (Tf₂N).

Overall, compound **3** presented a high thermal stability with a degradation temperature T_{onset} of 411 °C and a T_{peak} of 433 °C, thus belonging to the most stable level in the classification proposed by Cao and Mu (T_{onset} > 400 °C) [32].

Table 3. Start 5% ($T_{\text{start 5\%}}$), onset (T_{onset}), peak (T_{peak}), glass transition (T_g), crystallization (T_c), solid–solid transition (T_{s-s}), and melting (T_m) temperatures for compounds **1**, **2**, and **3**.

Compound		1	2	3
IL		C ₃ Br(C ₈ Im)/Br	C ₃ (C ₈ Im)(C ₁ Pyrr)/2 Br	C ₃ (C ₈ Im)(C ₁ Pyrr)/2 Tf ₂ N
TGA	$T_{\text{start 5\%}}$ (°C)	263.1	291.4	393.4
	T_{onset} (°C)	282.1	304.8	411.3
	T_{peak} (°C)	333.3	339.7	433.2
DSC	T_g (°C)	-50.3	-	-51.5
	T_m (°C)	-	113.7	-
	ΔH (KJ/mol)	-	13.61	-
	T_{s-s} (°C)	-	50.2(c)/50.3 (h)	-
	ΔH (KJ/mol)	-	-4.378 (c)/4.911 (h)	-
	T_c (°C)	-	101.2	-
	ΔH (KJ/mol)	-	-14.57	-

Differential scanning calorimetry (DSC) analysis of all synthesized compounds was also performed. All samples were analyzed at a scanning rate of 10 °C min⁻¹ under a nitrogen flow of 50 mL min⁻¹. The obtained glass transition (T_g), crystallization (T_c), solid–solid transition (T_{s-s}), and melting (T_m) temperatures are reported in Table 3. IL **1** and ADIL **3** displayed only a glass transition at -50.3 and -51.5 °C, respectively. Instead, bromide ADIL **2** presented a melting phenomenon (113.7 °C) associated to a crystallization event (101.2 °C) as well as two different solid–solid transitions (Figure S11 Supporting Information). Note that the melting temperature of **2** lies between that of the two symmetric bromide DILs: (C₃(C₈Im)₂/2 Br: T_m 173 °C [31]; C₃(C₁Pyrr)₂/2 Br: T_m 51 °C [18]).

3. Materials and Methods

3.1. General Information

¹H and ¹³C NMR spectra were recorded with a Bruker Advance II (Bruker Italia Srl, Milano, Italy) operating at 250.13 and 62.9 MHz at 24 °C. The first-order proton chemical shifts, δ , are referenced to either residual CD₃OD (δ_H 3.31, δ_C 49.03) or CDCl₃ (δ_H 7.26, δ_C 77.06), and J-values are given in Hz. The chemical shifts are given in δ . The following abbreviations are used; s = singlet, m = multiplet, bs = broad singlet, t = triplet, bt = broad triplet, q = quartet, qui = quintuplet, and sext = sextet.

TLC analyses were performed on Kieselgel 60 F254 with detection by UV light (254 nm) and/or with ethanolic 10% phosphomolybdic and heating. Kieselgel 60 (Merck, S.p.A., Milano, Italy, 230–400 mesh) was used for flash chromatography.

All reagents and solvents were obtained from Sigma Aldrich or Alfa Aesar and used without further purification. Na₂SO₄ was used as the drying agent for solutions.

Prior to TGA and DSC measurement, all samples were dried in high vacuum at 60 °C for 24 h to remove moisture and any volatile materials.

The thermal stability of the synthesized ILs was investigated by thermal gravimetric analysis (TGA), using a TA Instruments Q500 TGA (TA Instruments, New Castle, DE, USA). The temperature calibration was performed using nickel standard and for weight calibration was used a weight standards (1 g, 500 mg, and 100 mg). All standards were supplied by TA Instruments Inc. IL (15–20 mg) was heated in a platinum crucible as sample holder. IL was heated from 40 °C to 700 °C at 10 °C/min under nitrogen (90 mL/min). TGA experiments were carried out in triplicate.

The thermal behavior of the ionic liquids was analyzed by a differential scanning calorimeter TA Instruments DSC, Q250 (TA Instruments, New Castle, DE, USA). Dry high-purity N₂ gas with a flow rate of 30 mL/min was purged through the sample. The sample (5–10 mg) was loaded in hermetic aluminum crucibles and dried at 120 °C for 30 min. Then, the phase behavior was explored under nitrogen atmosphere in the temperature range of -90 to 200 °C with different heating rates. The temperature calibration for the different heating rates was performed considering the heating

rate dependence of the onset temperature of the melting peak of indium. The enthalpy was also calibrated using indium (melting enthalpy $\Delta_m H = 28.71$ J/g). DSC experiments were carried out in duplicate.

The dynamic viscosity of ionic liquids **1** and **3** was performed with a rheometer MCR 92 (Anton Paar, Ostfildern, Germany) equipped with a plate–plate geometry at 25 °C. The plate diameter was 25 mm with a gap of 0.05 mm. The viscosity was evaluated in rotation mode at 21 different shearing rates between 1 and 100 s⁻¹ after equilibration of 30 s.

Densities were determined using a glass pycnometer of nominal volumetric capacity of 3.00 cm³. The temperature was maintained at 25 °C using a thermostatic bath with a precision of ± 0.01 K. Density measurements were realized with an accuracy of at least ± 0.001 g/cm. The pycnometer was calibrated by ultra-pure toluene. All density measurements were repeated three times.

3.2. Synthesis of Ionic Liquid 1

Ionic liquid **1** was obtained following a general procedure previously reported [30]. To a solution of 1,3-dibromopropane (5 equivalents) in dry acetone (25 mL), a solution of *N*-octyl imidazole (1 equivalent, in 20 mL of dry acetone) was added. The reaction mixture was heated to 50 °C and stirred under nitrogen atmosphere for 24 h. The reaction was monitored by TLC (9:1 CH₂Cl₂–MeOH) analysis. After removal of acetone, the residual liquid was washed with diethyl ether (Et₂O, 30 mL) and then purified by silica column flash chromatography with dichloromethane/methanol (9:1, by vol) as eluent to afford compound **1** as a viscous liquid product (yield = 81%).

¹H NMR (CD₃OD) δ 9.11 (s, 1H, H-2), 7.70 (s, 2H, H-4, H-5), 4.42 (t, 2H, J_{vic} 7.5 Hz, CH₂N), 4.23 (t, 2H, J_{vic} 7.5 Hz, CH₂N), 3.49 (t, 2H, J_{vic} 7.5 Hz, CH₂Br), 2.45 (qui, 2H, J_{vic} 7.5 Hz, BrCH₂CH₂CH₂N), 1.97–1.80 (m, 2H, CH₂CH₂N), 1.43–1.18 (m, 10H, 5×CH₂ Chain), 0.96–0.81 (m, 3H, CH₃). ¹³C NMR (CD₃OD) δ 139.1 (C-2), 122.6, 122.4 (C-4, C-5), 51.7 (CH₂N), 49.6 (CH₂N), 32.0 (CH₂CH₂Br), 31.5 (CH₂CH₂N), 29.7 (BrCH₂CH₂CH₂N), 28.8, 28.7 (2×CH₂CH₂CH₂N), 28.2 (CH₂ chain), 25.9 (CH₂ chain), 22.3 (CH₂CH₃), 13.0 (CH₃). FTIR-ATR (cm⁻¹): 3381, 3063, 2954, 2925, 2855, 1562, 1456, 1247, 1163, 867, 751, 638. Degradation temperatures: 282 °C (onset), 333 °C (peak) (scanning rate = 10 °C/min). T_g = -50.3 °C (scanning rate = 10 °C/min).

3.3. Synthesis of Ionic Liquid 2

A solution of compound **1** (1 equivalent) in acetonitrile (4.0 mL) was mixed with an acetonitrile solution (2.0 mL) of *N*-methylpyrrolidine (2 equiv.). The reaction solution was heated to reflux and stirred under nitrogen for 96 h. At the end of the reaction, solvent and amine excess were evaporated under reduced pressure. The product was washed with diethyl ether (Et₂O, 3 × 10 mL) to afford the light yellow solid product **2** in a 96% yield.

¹H NMR (CD₃OD) δ 9.22 (s, 1H, H-2), 7.81, 7.71 (s, 2H, H-4, H-5), 4.42 (t, 2H, J_{vic} 7.5 Hz, CH₂N linker), 4.26 (t, 2H, J_{vic} 7.5 Hz CH₂N chain), 3.71–3.52 (m, 6H, CH₂N linker, 2× CH₂N Pyrr), 3.15 (s, 3H, CH₃N), 2.58–2.45 (m, 2H, NCH₂CH₂CH₂N), 2.34–2.17 (m, 4H, 2× CH₂CH₂ Pyrr), 1.99–1.86 (m, 2H, CH₂CH₂N), 1.47–1.21 (m, 10H, 5×CH₂ Chain), 0.90 (t, 3H, J_{vic} 7.5 Hz, CH₃). ¹³C NMR (CD₃OD) δ 137.6 (C-2 Im), 124.1, 123.8 (C-4, C-5 Im), 65.9 (2×CH₂N Pyrr), 61.8 (CH₂N linker Pyrr), 51.1 (CH₂N Linker Im), 49.4 (CH₃N), 47.6 (CH₂N), 32.9 (CH₂CH₂CH₃), 31.0 (CH₂CH₂N), 30.2, 30.1 (2×CH₂ chain), 27.3 (CH₂ chain), 25.9 (CH₂linker), 23.7 (CH₂CH₃), 22.6 (CH₂CH₂N Pyrr), 14.4 (CH₃). FTIR-ATR (cm⁻¹): 3449, 3391, 3076, 2988, 2957, 2923, 2854, 1565, 1454, 1410, 1360, 1232, 1165, 1007, 943, 748, 635. Degradation temperature: 305 °C (onset), 340 °C (peak) (scanning rate = 10 °C/min). T_m = 113.7 °C (scanning rate = 10 °C/min).

3.4. Synthesis of Ionic Liquid 3

A solution of **2** (1 equivalent) in water (6 mL) was added dropwise to an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (80% w/w, 1.2 equivalents). The resulting solution was stirred at room temperature for 3 h and then 10 mL of dichloromethane (CH₂Cl₂) was added. The organic phase was separated and washed with deionized water (3 × 10 mL). The absence of bromide

residue could be verified by using the AgNO_3 test. The resulting organic phase was dried over Na_2SO_4 , filtered, and the solvent was removed under reduced pressure. Product **3** was obtained as a yellow oil in a 98% yield.

^1H NMR ($\text{CD}_3\text{OD}/\text{CDCl}_3$) δ 8.83 (s, 1H, H-2), 7.57, 7.45 (s, 2H, H-4, H-5), 4.29 (t, 2H, J_{vic} 7.5 Hz CH_2N linker), 4.15 (t, 2H, J_{vic} 7.5 Hz, CH_2N chain), 3.60–3.38 (m, 6H, CH_2N linker, $2 \times \text{CH}_2\text{N}$ Pyrr), 3.04 (s, 3H, CH_3N), 2.48–2.34 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 2.32–2.13 (m, 4H, $2 \times \text{CH}_2\text{CH}_2$ Pyrr), 1.91–1.78 (m, 2H, $\text{CH}_2\text{CH}_2\text{N}$), 1.39–1.16 (m, 10H, $5 \times \text{CH}_2$ Chain), 0.85 (t, 3H, J_{vic} 7.5 Hz CH_3). ^{13}C NMR ($\text{CD}_3\text{OD}/\text{CDCl}_3$) δ 135.9 (C-2 Im), 125.0, 121.8, 118.6, 115.4 ($2 \times \text{CF}_3$ Tf₂N), 123.3, 123.2 (C-4, C-5 Im), 65.3 ($2 \times \text{CH}_2\text{N}$ Pyrr), 61.1 (CH_2N linker Pyrr), 50.7 (CH_2N Linker Im), 48.7 (CH_3N), 46.7 (CH_2N), 32.0 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 30.2 ($\text{CH}_2\text{CH}_2\text{N}$), 29.3, 29.2 ($2 \times \text{CH}_2$ chain), 26.6 (CH_2 chain), 25.3 (CH_2 linker), 22.9 (CH_2CH_3), 21.9 ($\text{CH}_2\text{CH}_2\text{N}$ Pyrr), 14.1 (CH_3). FTIR-ATR (cm^{-1}): 3152, 2932, 2861, 1565, 1467, 1347, 1178, 1133, 1051, 789, 740, 613, 569. Degradation temperature: 411 °C (onset), 433 °C (peak) (scanning rate = 10 °C/min). T_g = -51.5 °C (scanning rate = 10 °C/min).

4. Conclusions

In conclusion, we synthesized the ADIL 1-octyl-3-(3-(1-methylpyrrolidiniumyl)propyl)imidazolium bis(trifluoromethane)sulfonimide **3** in three steps in an excellent overall yield (76%). The final compound (**3**) and intermediates **1** and **2** were characterized by ^1H -NMR, ^{13}C -NMR, and FTIR to confirm their structure. The thermal stability of $\text{C}_3(\text{C}_8\text{Im})_2/2$ Tf₂N (**3**) was ascertained by TGA analysis, which confirmed this ADIL as a suitable medium for high thermal stability applications. The thermal behavior was evaluated by DSC to identify the specific operating range of all synthesized ILs. Viscosity at different share rates, solubility and density were also measured.

Further investigations of the physico-chemical properties of ADILs are necessary to identify structure–property correlations.

Supplementary Materials: The following are available online, NMR and FTIR spectra, viscosity, TGA and DSC analysis. Figures S1–S6: NMR spectra of compounds **1–3**, Figures S7–S9: TGA profiles of compounds **1–3**, Figures S10–S12: DSC thermographs of compounds **1–3**, Figures S13–S15: FT-IR spectra of compounds **1–3**, Figure S16: flow curves of compounds **1** and **3**.

Author Contributions: A.M. and L.G. conceived the work. A.M., C.S.P., and F.D.A. performed the experiments. A.M. and L.G. wrote the main text. All authors reviewed the manuscript.

Funding: This research received no external funding.

Acknowledgments: The authors would like to thanks Professor Maurizia Seggiani and Irene Anguillesi for their support in viscosity measurements.

Conflicts of Interest: The authors declare no conflicts of interest.

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