ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 11092–11094

www.rsc.org/chemcomm

COMMUNICATION

Poly(oxyalkylene) synthesis in Brønsted Acid Ionic Liquids†

Shaodong Zhang,[ab] Aurélie Féret,[ab] Hervé Lefebvre,[ab] Martine Tessier[ab] and Alain Fradet*[ab]

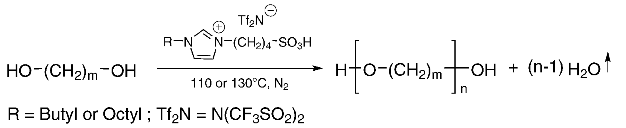
Received 11th July 2011, Accepted 2nd September 2011
DOI: 10.1039/c1cc14162g

The polyetherification of diols with 4–12 methylene units was studied in Brønsted Acid Ionic Liquids (BAILs). High molar mass poly(oxyalkylene)s were obtained at relatively low temperatures (130 °C), except in the cases of 1,4-butanediol and 1,6-hexanediol where cyclic ether formation was observed.

Poly(oxyalkylene)s are generally synthesized by the ring-opening polymerization of the corresponding cyclic ethers, such as oxiranes,[1,2] oxetanes,[3] THF[4] and oxepane.[5] However, tetrahydropyran (cyclic ether with 5 methylene units) does not homopolymerize[6] and the polymerization of cyclic ethers with 7 or more methylene units still remains largely unknown. Another polyether synthetic method is based on the Williamson reaction between activated diols and dihalides or involving monomers with both hydroxy and halide groups.[7–9] However, this method is rather ineffective when dealing with aliphatic diols.[10] It is also reported that Williamson polyetherifications can be carried out under heterogeneous conditions with phase-transfer catalysts,[11–15] but polyethers precipitate during the reactions, which inevitably limits the formation of high molar mass polyethers.

In the early 1950s, Rhoad and Flory[16] reported the self-condensation of 1,10-decanediol and of benzylic diols. In their pioneering work, polyethers were synthesized in bulk, in the presence of sulfamic or sulfuric acids at elevated temperature (200–300 °C). Later on, Kobayashi *et al.*[17] also conducted the synthesis of linear poly(oxyalkylenes) with the same method in the presence of H_2SO_4 and $(C_2H_5)_2O{\cdot}BF_3$. No polymer molar mass was reported in their works. These results encouraged our research on direct polyetherification of different dialcohols carried out in Brønsted Acid Ionic Liquids (BAILs), as to the latter a burgeoning attention has been paid in recent years. BAILs are non-volatile, easily recyclable reaction media of high thermal and chemical stabilities,[18–21] which can be used as both an alternative of organic solvent and catalyst for acid-catalyzed reactions.[22–25]

In this communication, we report, to the best of our knowledge, the first direct polyetherification of different aliphatic diols in BAILs, namely 4-(3′-butyl-1′-imidazolio)-1-butanesulfonic acid bis(trifluoromethylsulfonyl)imidide and 4-(3′-octyl-1′-imidazolio)-1-butane-sulfonic acid bis(trifluoromethylsulfonyl)imidide, [BBSIm]Tf$_2$N and [OBSIm]Tf$_2$N, respectively. High molar mass polyethers were produced according to Scheme 1 in these two BAILs, which served as both reaction medium and catalyst.



Scheme 1 Synthesis of linear polyether in 4-(3′-butyl-1′-imidazolio)-1-butanesulfonic acid bis(trifluoromethylsulfonyl)imidide ([RBSIm]Tf$_2$N), $m > 6$.

A preliminary study on the direct polyetherification of 1,12-dodecanediol was conducted in the two BAILs, under various experimental conditions (Table 1). The influence of temperature was first studied and, as expected for a kinetically controlled polymerization, reactions were slower at lower temperatures, as the molar masses of final products were only about 7000–8000 at 110 °C (entries 1 and 2). However, when the reaction was carried out at 130 °C, high molar mass polyethers were produced, as molar mass increased to *ca.* 23 000 (entries 3 and 4). It seems that the length of the alkyl substituent of imidazolium-based ionic liquids does not necessarily have an impact on 1,12-dodecanediol polyetherification. For example, when polyetherification was carried out in the two BAILs at 110 °C, no significant difference was observed between the molar masses or polydispersities of resulting polyethers (entries 1 and 2). The same tendency was observed at 130 °C (entries 3 and 4).

The influence of initial diol concentration on polyetherification was also examined. No significant molar mass variation was observed when the monomer/BAIL molar ratio increased from 2 : 1 to 3 : 1 (entries 4 and 5), though it was found that the viscosity of the reaction media increased. On the other hand, when the molar ratio decreased to 1 : 1 (entries 6 and 7), even though the reactions were maintained for a longer time (70 to 96 hours), the molar masses of resulting poly(oxydodecamethylene)s were only 12 000 and 14 000, which shows that the reaction is less effective in a diluted medium. The polydispersity index (PDI) of the polyethers obtained with 2 : 1 molar ratio was close to 2, which is the theoretical PDI value for polycondensation polymers with the most probable distribution of molar masses. Whatever the experimental conditions, the molar mass was limited to 23 000, which may be due to diffusion control of the kinetics when reaction medium viscosity increases with chain growth or to the existence of side reactions during the polymerization.

---

[a] *UPMC Univ. Paris 06, UMR 7610, Laboratoire de Chimie des Polymères, Courrier 184, 94200 Ivry sur Seine, France. E-mail: alain.fradet@upmv.fr*
[b] *CNRS, UMR 7610, Laboratoire de Chimie des Polymères, Courrier 184, 4 Place Jussieu, 75005 Paris, France*

† Electronic supplementary information (ESI) available: Experimental part, ^{1}H–^{1}H COSY-45 2D-NMR and ^{19}F NMR spectra, DSC thermograms. See DOI: 10.1039/c1cc14162g

Table 1 Polyetherification of 1,12-dodecanediol in BAILs under N_2 flow (200 ml min^{-1}): mass-average molar mass (M_w) and polydispersity index (PDI) calculated from SEC data and melting points (T_m) measured by DSC

Entry	BAIL	Temperature/°C	Monomer/BAIL^a (mol/mol)	Time/h	Yield^b (%)	M_w/g mol^{-1}	PDI	T_m/°C	$T_m{}^c$/°C
1	[OBSIm]Tf_2N	110	2/1	63	73.2	8000	1.9	76.7	72–73
2	[BBSIm]Tf_2N	110	2/1	63	72.0	7300	1.9	72.6	72–73
3	[BBSIm]Tf_2N	130	2/1	63	85.7	22 000	2.2	79.1	72–73
4	[OBSIm]Tf_2N	130	2/1	63	71.2	23 000	2.4	79.6	72–73
5	[OBSIm]Tf_2N	130	3/1	65	72.6	21 000	3.8	77.2	72–73
6	[OBSIm]Tf_2N	130	1/1	96	69.0	12 000	4.4	75.4	72–73
7	[BBSIm]Tf_2N	130	1/1	70	63.8	14 000	3.7	75.2	72–73

^{a} Initial monomer ratio between monomer and BAIL. ^{b} Isolated yield. ^{c} Melting point from the literature.[16]

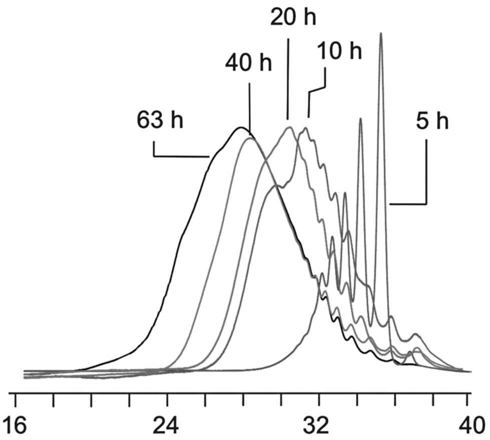


Fig. 1 Polyetherification of 1,12-dodecanediol in [BBSIm]Tf_2N at 130 °C under N_2 flow (200 ml min^{-1}), diol/BAIL = 2/1: SEC chromatograms (CH_2Cl_2, 1.0 ml min^{-1}) after 5, 10, 20, 40, 63 h reaction.

The influence of reaction time on 1,12-dodecanediol polyetherification in [BBSIm]Tf_2N was also studied (Fig. 1). It was found that the molar mass increased almost proportionally with time between 10 h to 40 h (M_w = 6000–20 000 g mol^{-1}). At longer reaction times, the molar mass grew slowly until M_w = 22 000 g mol^{-1} for 63 h.

The ^{1}H NMR spectra of purified poly(oxydodecamethylene)s present the expected repeating unit main peaks and no OH end-group resonance (CH_2–OH at 3.6 ppm). However, they present a peak of very low intensity at 5.4 ppm, together with other resonances ($H^{1,2,5,1''}$, Fig. 2), which was assigned to unsaturations by 2D ^{1}H–^{1}H NMR (see ESI†). It appears that H^+-catalyzed OH end-group dehydration side reaction takes place, followed by carbocation migration, leading to the formation of double bonds in α, β and γ positions to the original OH group (Scheme 2).

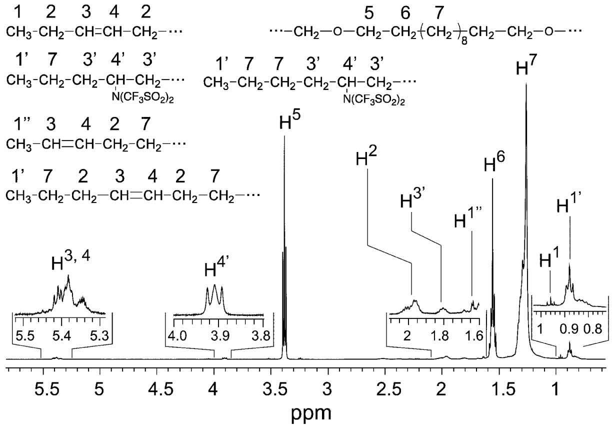
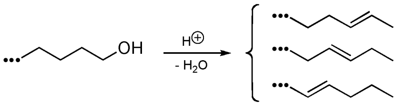
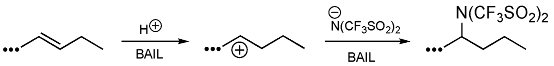


Fig. 2 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of purified poly(oxydodecamethylene), reaction undertaken at 130 °C, diol/BAIL = 2/1, 63 h in [OBSIm]Tf_2N under N_2 flow (200 ml min^{-1}).



Scheme 2 Dehydration of alcohol end groups in BAILs.



Scheme 3 Hydroamination of double bonds in the γ position by Tf_2N^- in BAILs.

The ^{1}H NMR spectra also present small resonances at 3.9 and 1.8 ppm ($H^{3',4'}$, Fig. 2), which were assigned to the hydroamination of double bonds in γ (Scheme 3) and/or δ positions. According to Kuhnert *et al.*,[26] double bonds can be hydroaminated by Tf_2NH under acidic conditions. The ^{19}F NMR spectrum of this product presents a new resonance at −75.2 ppm, different from that of the Tf_2N^- counterion in the BAIL at −80.0 ppm, which is a further indication of the hydroamination. These two side reactions could also explain why polymer molar mass was limited at the later stages of reaction.

Nevertheless, it was found that high molar mass polyethers could be obtained in either [BBSIm]Tf_2N or [OBSIm]Tf_2N with an initial molar ratio of 2 : 1 (monomer : IL) at 130 °C. The same conditions were therefore used to study the polyetherification of other aliphatic diols in these two BAILs.

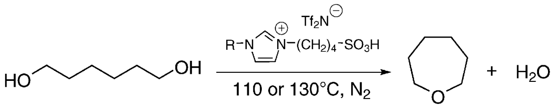
Table 2 shows that high molar mass polyethers could also be synthesized from the diols with 7 to 10 methylene units. Polyethers could not be produced from 1,6-hexanediol or 1,4-butanediol in these two BAILs, but oxepane and THF were detected, respectively, from their reaction media. It appears that the formation of cyclic ethers of 1,4-butanediol and 1,6-hexanediol rather than polyetherification was favored under the same conditions in the BAILs, as volatile products were distilled from the reaction media, which were, respectively, THF and oxepane (Scheme 4).

As a conclusion, we have demonstrated for the first time that, in [BBSIm]Tf_2N or [OBSIm]Tf_2N BAILs, high molar mass linear polyethers can be synthesized by a simple direct polyetherification of diols with 7 to 12 methylene units. On the

Table 2 Polyetherification of different aliphatic diols in BAILs with diol/BAIL (mol/mol) = 2/1 at 130 °C under N_2 flow (200 min ml^{-1}): mass-average molar mass (M_w) and polydispersity index (PDI) calculated from SEC data, melting point measured by DSC

Entry	BAIL	Monomer	Time/h	Yield[a] (%)	M_w/g mol^{-1}	PDI	T_m/°C	$T_m{}^b$/°C
8	[OBSIm]Tf_2N	1,10-Decanediol	50	65.0	25 500	2.3	73.8	75–79
9	[OBSIm]Tf_2N	1,9-Nonanediol	60	61.1	23 900	2.3	69.5	71–73
10	[OBSIm]Tf_2N	1,8-Octanediol	50	73.2	26 700	2.6	73.0	64–67
11	[BBSIm]Tf_2N	1,8-Octanediol	50	77.3	42 000	2.2	68.4	64–67
12	[BBSIm]Tf_2N	1,7-Heptanediol	60	56.2	20 400	2.0	50.6	—
13[c]	[RBSIm]Tf_2N	1,6-Hexanediol	60	—	—	—	—	55–58
14[c]	[RBSIm]Tf_2N	1,4-Butanediol	60	—	—	—	—	43

[a] Isolated yield. [b] Melting point from the literature.[17] [c] Only oligomers were formed in either [BBSIm]Tf_2N or [OBSIm]Tf_2N.



Scheme 4 Formation of oxepane in [RBSIm]Tf_2N, R = octyl or butyl.

other hand, cyclic ethers of 1,6-hexanediol and 1,4-butanediol rather than polyethers were formed under the same conditions, which could be another method for cyclic ether synthesis.

Notes and references

1 S. Perry and H. Hibbert, *J. Am. Chem. Soc.*, 1940, **62**, 2599–2604.
2 E. J. Vandenberg, *J. Polym. Sci.*, 1960, **47**, 486–489.
3 O. Moriya, S.-i. Yamamoto, T. Sugizaki, J. Maeda, A. Kamejima, T. Kumon and T. Kageyma, *Polym. J. (Tokyo)*, 2005, **37**, 262–269.
4 M. P. Dreyfuss and P. Dreyfuss, *Polymer*, 1965, **6**, 93–95.
5 T. Saegusa, T. Shiota, S.-i. Matsumoto and H. Fujii, *Macromolecules*, 1972, **5**, 34–36.
6 S. Inoue and T. Aida, in *Ring-opening polymerization*, ed. K. J. Ivin and T. Saegusa, Elsevier Applied Science Publishers, Barking, 1984, vol. 1.
7 J. Lal and G. S. Trick, *J. Polym. Sci.*, 1961, **50**, 13–19.
8 K. E. Uhrich, C. J. Hawker and J. M. J. Frechet, *Macromolecules*, 1992, **25**, 4583–4587.
9 J. Maslinska-Solich, S. Kukowka and P. Markowski, *React. Funct. Polym.*, 2008, **68**, 544–556.
10 M. Jayakannan and S. Ramakrishnan, *Macromol. Chem. Phys.*, 2000, **201**, 759–767.
11 L. Li, C.-M. Chan, K.-M. Ng, Y. Le and L.-T. Weng, *Polymer*, 2001, **42**, 6841–6849.
12 P. Keller, *Makromol. Chem. Rapid Commun.*, 1985, **6**, 255–259.
13 V. Percec, P. Chu and M. Kawasumi, *Macromolecules*, 1994, **27**, 4441–4453.
14 V. Percec and M. Kawasumi, *Macromolecules*, 1991, **24**, 6318–6324.
15 S. Chatti, M. Bortolussi, A. Loupy, J. C. Blais, D. Bogdal and M. Majdoub, *Eur. Polym. J.*, 2002, **38**, 1851–1861.
16 M. J. Rhoad and P. J. Flory, *J. Am. Chem. Soc.*, 1950, **72**, 2216–2219.
17 S. Kobayashi, H. Tadokoro and Y. Chatani, *Makromol. Chem.*, 1968, **112**, 225–241.
18 T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2083.
19 M. J. Earle and K. R. Seddon, *Pure Appl. Chem.*, 2000, **72**, 1391.
20 K. R. Seddon and R. D. Rogers, *Science*, 2003, **302**, 792.
21 J. S. Wilkes, P. Wasserscheid and T. Welton, in *Ionic Liquids in Synthesis*, ed. P. Wasserscheid and T. Welton, Wiley-VCH Verlag GmBH, Weinheim, 2nd edition, 2008, **vol. 1**, pp. 1–6.
22 A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes and J. H. Davis Jr., *J. Am. Chem. Soc.*, 2002, **124**, 5962–5963.
23 S. Dali, H. Lefebvre, R. E. Gharbi and A. Fradet, *e-Polymers*, 2007, **65**.
24 J. Shen, H. Wang, H. Liu, Y. Sun and Z. Liu, *J. Mol. Catal. A: Chem.*, 2008, **280**, 24–28.
25 E.-M. Dukuzeyezu, H. Lefebvre, M. Tessier and A. Fradet, *Polymer*, 2010, **51**, 1218–1221.
26 N. Kuhnert, J. Peverley and J. Robertson, *Tetrahedron Lett.*, 1998, **39**, 3215–3216.