

Polymer Communication

Synthesis of high molar mass poly(12-hydroxydodecanoic acid) in brønsted acid ionic liquids

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ABSTRACT

An easy and fast direct polyesterification method using Brønsted acid ionic liquids (BAILs) as both reaction medium and catalyst was investigated. High molar mass polyesters of 12-hydroxydodecanoic acid (up to $\overline{M}_w = 50,000 \text{ g mol}^{-1}$) were obtained in good yields at atmospheric pressure and low temperature (90–130 °C) after 10–120 min reaction and without any added catalyst, reaction conditions that are much milder than conventional ones. Ionic liquids composed of an acidic cation bearing sulfonic acid groups and an acidic anion, such as 3-alkyl-1-(butyl-4-sulfonyl)imidazolium hydrogen sulfates, gave better results than ionic liquids containing only an acidic anion, such as 1-alkyl-3-methylimidazolium hydrogen sulfates. The 1/1 BAIL/12-hydroxydodecanoic acid molar ratio was found to yield polymers of the highest molar mass.

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1. Introduction

Polyesters are usually synthesized by reaction between diols and diacids or diesters. In order to achieve high conversions and to obtain high-molar-mass polyesters in reasonable reaction time, such reactions are usually carried out in the bulk, at high temperature and in the presence of protonic acid or organometallic catalysts. The process requires several hours heating at high temperature (>200 °C) and vacuum is often applied at the end of reaction to distil off the last traces of by-product from the viscous reaction medium, in order to shift esterification equilibrium toward polymer formation [1].

Such harsh conditions favour side reactions that can lead to uncontrolled molar masses, architectures and microstructures. Alternatively, high-molar-mass polyesters can be obtained by solution reactions of acid chlorides or activated carboxylic acids and diols in milder conditions and shorter time without interchange or degradation side reactions. However, the formation of high amount of cyclic species and the difficulty to control molar mass are serious disadvantages. The use of expensive and/or toxic starting reactants and solvents are additional drawbacks. Removing and/or replacing volatile and harmful solvents as well as saving energy and time are

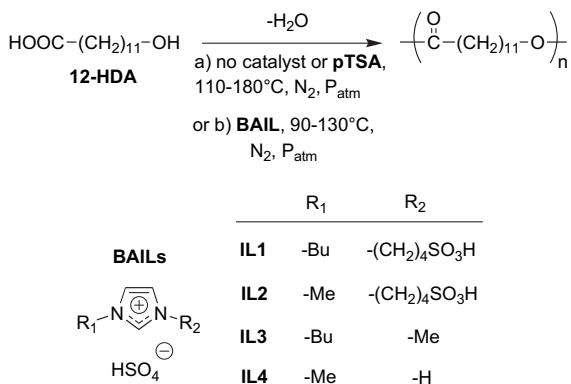
the challenges of green process research. In this context, ionic liquids (IL)s have appeared as interesting novel polymerization reaction media [2], owing to their unique properties: negligible vapor pressure, high thermal and chemical stabilities, non-flammability and reusability [3–5].

Some authors reported on polycondensation reactions in ionic liquids [6–11]. A few studies were undertaken on the synthesis of polyesters in ionic liquids, mainly in dialkylimidazolium bis(trifluoromethylsulfonyl)amide salts. Enzymatic methods [12,13] yielded low molar mass polyesters, poly(glycolic acid) and poly(L-lactic acid) were obtained by post-polycondensation of oligomers [14,15] and the copolymerization of oligo(glycolic acid) with ϵ -caprolactone led to soluble copolyesters [16]. Liu and co-workers [17] showed that high molar mass polyesters can be obtained in dialkylimidazolium bis(trifluoromethylsulfonyl)amide salts by post-polycondensation of oligoesters, but the two-step procedure required high temperature reaction (160 °C), reduced pressure (50 Pa), long reaction time (24 h) and the addition of a metal catalyst. Brønsted acid ionic liquids (BAILs) are a class of ionic liquids that can be used as solvent and/or acid catalyst for the protection of carbonyl groups, the condensation of phenols and the synthesis of esters [18–27]. However, to date no polyesterification reaction has been undertaken in these ionic liquids.

In this article, we report on the first direct polyesterifications undertaken in Brønsted acid ionic liquids (BAILs) at low to moderate temperature (90–130 °C), atmospheric pressure and without any added catalyst. The polyesterification of 12-hydroxydodecanoic

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Scheme 1. Polyesterification of 12-HDA in BAILs.

acid (12-HDA) was investigated using 3-alkyl-1-(butyl-4-sulfonyl)imidazolium hydrogen sulfates and 3-alkyl-1-(butyl)imidazolium hydrogen sulfates as both reaction media and catalysts. The effect of reaction time and temperature, nitrogen flow rate and BAILs/12-HDA molar ratio on average molar masses and yields was investigated.

2. Experimental part

2.1. Chemicals

1-butylimidazolium (purity grade 98%), 1,1-butanedisulfone (purity grade $\geq 99\%$), 12-hydroxydodecanoic acid (12-HDA, purity grade 97%), *p*-toluenesulfonic acid monohydrate (*p*-TSA, purity grade $> 98.5\%$) and 1-methylimidazolium hydrogen sulfate (IL4, purity grade $> 95\%$) were purchased from Aldrich (Saint-Quentin Fallavier, France). 1-methylimidazolium (purity grade 98%) was purchased from Acros (Halluin, France). 1-butyl-3-methylimidazolium hydrogen sulfate (IL3, purity grade $> 98\%$) was obtained from Solvionic (Toulouse, France). All chemicals and solvents were used as received.

2.2. Synthesis of ionic liquids

3-butyl-1-(butyl-4-sulfonyl)imidazolium hydrogen sulfate (IL1) and 3-methyl-1-(butyl-4-sulfonyl)imidazolium hydrogen sulfate (IL2) were synthesized according to known procedures [22,27].

2.3. Polyesterification in ionic liquid

The general procedure is described below with an example:

A 15 mL glass tube equipped with a nitrogen inlet and outlet containing 1.0 mmol 3-butyl-1-(butyl-4-sulfonyl)imidazolium hydrogen sulfate IL1 (358 mg) and 1.0 mmol 12-hydroxydodecanoic acid (12-HDA) (216 mg) was placed in an oil bath at

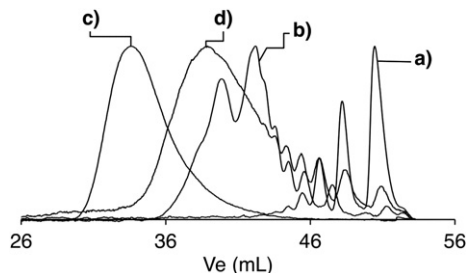


Fig. 1. Polyesterification of 12-HDA at 110 °C a) in the bulk without catalyst, b) in the bulk in the presence *p*-toluenesulfonic acid (12-HDA/*p*-TSA molar ratio = 1/1) c) in ionic liquid IL1 (12-HDA/IL1 molar ratio = 1/1) and d) at 180 °C without catalyst (N₂ flow rate = 500 mL/min); SEC chromatograms (CH₂Cl₂, 1.0 mL/min) after 120 min reaction.

110 °C under magnetic stirring. A 500 mL min⁻¹ nitrogen flow rate was applied over reaction medium. After 120 min reaction, 10 mL of isopropyl alcohol was introduced and heated at reflux for 5 min and then cooled down to room temperature under magnetic stirring. The polyester was recovered by filtration and washed with isopropyl alcohol and diethyl ether. Yield 87%. The yield was calculated by dividing the recovered mass by the starting mass of 12-HDA.

¹H NMR (CDCl₃, 300 MHz): 4.05 (2H, t, -CH₂-O-CO-); 3.63 (2H, t, -CH₂-OH); 2.34 (2H, t, -CH₂-COOH); 2.28 (2H, t, -CH₂-COO-); 1.60 (4H, m, -CH₂-CH₂-O-CO- and -CH₂-CH₂-CO-O-); 1.27 (14H, m, -(CH₂)₇-CH₂-CH₂-O-) T_m (DSC): 83,1 °C; ΔH_m (DSC): 13,60 J g⁻¹; T_{10%} (TGA): 380 °C

2.4. Analytical methods

NMR Spectroscopy: ¹H NMR spectra were recorded on Bruker Avance 250 or 300 MHz spectrometers in CDCl₃ solutions (ref. δ(CHCl₃) = 7.26 ppm) or in DMSO-d₆ solutions (ref. δ(DMSO) = 2.50 ppm).

Size Exclusion Chromatography (SEC): The SEC chromatograms were recorded at room temperature on a Waters equipment consisting of a 410 refractive index detector, a 515 HPLC pump and a set of Ultrastaygel columns (100+500+10³+10⁴+10⁵ Å) in CH₂Cl₂ at a flow rate of 1.0 mL/min. Polystyrene standards were used to calibrate the system.

Thermogravimetric Analyses (TGA) were carried out on a TA-Instrument Q50 thermogravimetric analyzer at a heating rate of 20 °C/min in flowing nitrogen.

Differential Scanning Calorimetry (DSC) was performed on a TA-Instrument DSC 2010 apparatus following heating/cooling cycle: (1) cooling to -120 °C (2) heating from 20 °C to 140 °C at 20 °C/min, (3) cooling to -120 °C at 10 °C/min. (4) heating from -120 °C to 140 °C at 20 °C/min. The melting points (T_m), taken at the minima of the melting endotherms, and the glass transition temperatures (T_g),

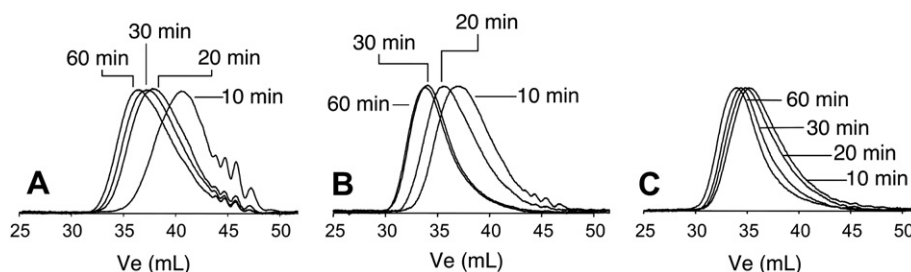


Fig. 2. Polyesterification of 12-HDA in ionic liquid IL1 at A) 90 °C, B) 110 °C and C) 130 °C (12-HDA/IL1 molar ratio = 1/1; N₂ flow rate = 500 mL min⁻¹); SEC chromatograms (CH₂Cl₂, 1.0 mL/min) after 10, 20, 30 and 60 min reaction.

taken at the inflection points, were obtained from the second heating run.

3. Results and discussion

One of the most common methods for the synthesis of aliphatic polyester is the high temperature (180–220 °C), low-pressure bulk polycondensation that requires catalyst, long reaction time (5–7 h) and vacuum [1]. In this work, we compare the polymerization of 12-hydroxydodecanoic acid (12-HDA) (i) in the bulk without catalyst, (ii) in the bulk in the presence of *p*-toluenesulfonic acid (*p*-TSA), a well known polyesterification catalyst, and (iii) in several Brønsted acid ionic liquids (BAILs) (Scheme 1).

In all cases, the polymerizations were undertaken at atmospheric pressure, under a controlled nitrogen flow. Fig. 1 shows the SEC chromatograms corresponding to the polymerization of 12-HDA without catalyst at 110 °C and 180 °C and with *p*-TSA catalyst at 110 °C. As can be seen, at 110 °C without catalyst, only oligomers were obtained after 120 min reaction (trace (a)). When the reaction was carried out at 180 °C oligomers of $\overline{M}_n < 4000$ g mol⁻¹ were obtained (trace (d)). The addition of *p*-TSA at 110 °C afforded a low molar mass oligomer ($\overline{M}_n < 700$ g mol⁻¹, trace (b)). On the other hand, the polyesterification of 12-HDA in 3-butyl-1-(butyl-4-sulfonyl)imidazolium hydrogen sulfate (IL1) yielded a high molar mass poly(12-hydroxydodecanoic acid) ($\overline{M}_n = 18,900$ g mol⁻¹, trace (c)). It should be pointed out that 12-HDA and its low molar mass oligomers are soluble in IL1, but, during polyesterification, molten poly(12-hydroxydodecanoic acid) separates from the ionic liquid and, under stirring, the solution turns into an emulsion. Upon cooling, poly(12-hydroxydodecanoic acid) solidifies and can be recovered by filtration and washing with water, ethanol or isopropanol. The addition of isopropanol in the hot reaction medium followed by cooling to room temperature facilitated the separation of poly(12-hydroxydodecanoic acid) as a fine white powder.

The effect of temperature on the polyesterification of 12-HDA in IL1 is illustrated in Fig. 2. Even at a temperature as low as 90 °C, polymerization occurred rapidly. After only 10 min reaction, a polyester of $\overline{M}_n = 6800$ g mol⁻¹ was obtained. After 20 min reaction, the molar mass almost doubled and reached $\overline{M}_n = 39,000$ g mol⁻¹ after 120 min (Table 1). At higher temperatures, the SEC curves are shifted to higher molar masses, which indicates higher polymerization rate. At 110 °C and 130 °C, poly(12-hydroxydodecanoic acid) of $\overline{M}_n = 13,600$ and 23,000 g mol⁻¹, respectively, were obtained after 10 min reaction and poly(12-hydroxydodecanoic acid) of $\overline{M}_n = 35,800$ and 30,700 g mol⁻¹

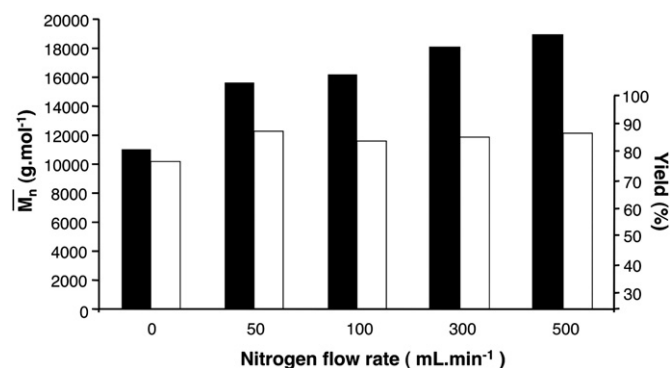


Fig. 3. Polyesterification of 12-HDA at 110 °C for 120 min in ionic liquid IL1 (12-HDA/IL1 molar ratio = 1/1) under various nitrogen flow rates: Variation of (■) the number average molar mass calculated by ¹H NMR and of (□) yield versus nitrogen flow rate.

after 30 min reaction. Table 1 shows that after 120 min reaction, high molar mass polyesters were obtained in good yields in all cases.

The effect of 12-HDA/BAIL molar ratio was studied between 1/3 and 3/1 at 110 °C (P2 and P4–P7, Table 1). The highest molar mass ($\overline{M}_w = 40,200$ g mol⁻¹) was obtained for the 1/1 molar ratio. Both more diluted and more concentrated reaction media resulted in polyesters of lower molar mass. This can be explained by two antagonist effects: (i) The classical effect of dilution on reaction rate, lower monomer concentration leading to slower reaction rate and (ii) the effect of medium viscosity on reaction rate: High monomer concentration resulted in highly viscous reaction medium, in which the formation of high molar mass species could be hindered by diffusion phenomena. The poly(12-hydroxydodecanoic acid) of the highest molar mass ($\overline{M}_w = 46,000$ g mol⁻¹) was obtained at 150 °C with 1/2 12-HDA/IL1 molar ratio. In this case, the unfavorable effect of dilution on kinetics and molar mass is clearly counterbalanced by the higher reaction temperature and its effect on reaction rate related to the activation energy of the process.

The results obtained on P2 and P10–P12 samples (Table 1) reflect the influence of BAIL structure. 3-Methyl-1-(butyl-4-sulfonyl)imidazolium hydrogen sulfate (IL2) yielded a polyester of $\overline{M}_w = 16,000$ g mol⁻¹, lower than that of obtained in IL1 probably because of the higher viscosity of reaction medium. 1-Methylimidazolium hydrogen sulfate (IL4) and 1-butyl-3-methylimidazolium hydrogen sulfate (IL3) gave homogeneous reaction media but only low yields of oligomers were obtained. These BAILs, which do not contain sulfonic acid group, are less acidic and therefore do not catalyze polyesterification as effectively as IL1 and IL2.

Table 1
Polyesterification of 12-HDA in Brønsted acid ionic liquids (BAILs) for 120 min (N₂ flow rate = 500 mL min⁻¹): Mass-average molar mass (\overline{M}_w), molar mass at the maximum of SEC curve (M_{peak}) and polydispersity index (PDI) from SEC data; number-average degree of polymerization (\overline{DP}_n) and molar mass (\overline{M}_n) from NMR data; Yield (%).

Sample	T ^a (°C)	BAIL	12-HDA/BAIL mol ratio	M _{peak} ^b g mol ⁻¹	\overline{M}_w ^b g mol ⁻¹	PDI ^b	\overline{DP}_n ^c	\overline{M}_n ^c g mol ⁻¹	Yield ^d %
P1	90	IL1	1/1	40,000	39,000	2.20	75.8	15,100	91
P2	110	IL1	1/1	43,500	40,200	2.11	95.1	18,900	87
P3	130	IL1	1/1	49,900	44,200	2.04	97.9	19,400	83
P4	110	IL1	3/1	18,600	17,800	2.21	38.4	7600	86
P5	110	IL1	2/1	28,200	26,900	2.14	44.7	8900	84
P6	110	IL1	1/2	38,000	33,400	2.23	50.9	10,100	82
P7	110	IL1	1/3	31,500	30,200	2.07	61.4	12,200	82
P8	130	IL1	1/2	32,400	29,300	2.29	56.9	11,300	79
P9	150	IL1	1/2	50,400	46,000	2.20	103.9	20,600	89
P10	110	IL2	1/1	33,500	16,100	2.06	58.0	11,500	86
P11	110	IL3	1/1	<1000	<1000	–	–	<1000	–
P12	110	IL4	1/1	<700	<700	–	–	<700	–

^a Reaction temperature.

^b Values from SEC in CH₂Cl₂.

^c Values from ¹H NMR (CDCl₃).

Fig. 3 illustrates the effect of nitrogen flow rate on the number average molar mass and on polyester yield. The reaction proceeded smoothly even without nitrogen flow and afforded a poly(12-hydroxydodecanoic acid) of $\overline{M}_w = 24,600 \text{ g mol}^{-1}$. The introduction of a nitrogen flow over reaction medium facilitated the elimination of reaction water and shifted the polycondensation equilibrium toward the formation of high molar mass polyesters, increasing flow rates leading to higher molar mass polyesters.

4. Conclusion

A new method for the synthesis of polyesters, using Brønsted acid ionic liquids both as solvent and catalyst, was investigated. The polyesterification of 12-hydroxydodecanoic acid in sulfonic acid group-containing ionic liquids can yield high molar mass poly(12-hydroxydodecanoic acid) at low to moderate temperature (90–130 °C) in short reaction time (30–60 min) and at atmospheric pressure, reaction conditions that are considerably milder than conventional ones (5–7 h, 180–220 °C, vacuum). The presence of a nitrogen flow shifted the polycondensation reaction equilibrium toward the formation of high molar mass polyesters.

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