Reactive & Functional Polymers 72 (2012) 133–141

Contents lists available at SciVerse ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

Synthesis and characterization of imidazolium telechelic poly(butylene terephthalate) for antimicrobial applications

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ARTICLE INFO

Article history:
Received 14 October 2011
Received in revised form 28 November 2011
Accepted 4 December 2011
Available online 8 December 2011

Keywords:
Imidazolium salt
Telechelic
Ionomer
Polyester
Antimicrobial properties

ABSTRACT

Poly(butylene terephthalate) ionomers with imidazolium groups selectively located as end-groups (telechelic) have been prepared by melt polycondensation adding a hydroxyl derivatized imidazolium salt at the beginning of the polymerization process. The design of the chemical structure of the imidazolium salt is of fundamental importance in order to achieve the synthesis of ionomers with good thermomechanical properties. The final ionomers present high molecular weight, good color, transparency and thermal stability. Imidazolium ionomers present good antimicrobial (AM) properties comparable with those of commercial AM agents. The incorporation of the ionic groups in the polymer chain prevents their migration during use and therefore the antimicrobial activity can be preserved for longer time.

1. Introduction

Imidazolium salt derivatives have been used in the last few years in several biological and material science applications. For example, a recent review [1] reports that polyimidazoles can be used as oxygen transport membranes [2] or as scaffold for biomimetic applications [3]. Imidazolium ionomers can also be used to create polyelectrolyte brushes [4], coat metal nanoparticles [5] and produce oriented liquid crystals [6]. Moreover, imidazolium salts have proved to be very active as microbicidal agents [7,8]. The effect of substituents of the imidazolium moiety on the antibacterial activity of imidazolium salts has been reported in the literature [8]. In particular, imidazolium salts bearing long alkyl chains (with 15–18 methylene groups) present the stronger bactericidal properties [8].

Imidazolium derivatives have been used in most applications as additives blended with the polymer matrix [7]. However, the use of antimicrobial agents blended in a polymer matrix can give rise to the migration towards the surface of the antibacterial agent and therefore the antimicrobial activity decreases during the lifetime of the polymer application such as fiber or molded article. For this reason, in the last years, several research groups have tested the use of antimicrobial agents covalently bonded to the polymer chain [9]. For example, Chen et al. [10] described the surface grafting polymerization of N-vinyl-2-pyrrolidone onto poly(ethylene terephthalate) by plasma pretreatment with silver nanoparticles. Konagaya et al. [11] have reported the preparation of antibacterial acrylic acid-grafted copolyesters with phosphonium salts. Cen et al. [12] studied a surface functionalization technique for conferring antibacterial properties to polymeric and cellulosic surfaces, using a pyridinium salt grafted by copolymerization. Other researchers have reported [13] the use of vinyl pyridine grafted with alkyl chains. Other studies [14] pointed out that hexadecyl alkyl chains bonded to diazobicyclooctane (DABCO) are active against bacteria. The synthesis of polyaramides with pendant alkyl ammonium groups that mimic peptide groups is also described in the literature [15]. However, quaternary ammonium cations are not stable enough to be incorporated in a terephthalate polyester chain since they are subjected to degradation reactions at the normal synthesis and processing conditions of such polyesters. On the contrary, imidazolium cations have a consistently higher thermal stability. For example, clays modified with imidazolium cations are stable at temperature exceeding 300 °C while those modified with ammonium salts start degrading below 240 °C [16]. It is important to note that the counterion severely affects the thermal stability of

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doi:10.1016/j.reactfunctpolym.2011.12.003

imidazolium salts. It is reported in the literature [17] that tetrafluoroborate salts (BF_4^-) and hexafluorophosphate salts (PF_6^-) are much more stable than chloride and bromide salts.

Ionic groups can be inserted in the polymer chains selectively at the chain ends (telechelic ionomers) or randomly distributed along the polymer chain (random ionomers) [18–21]. The position of the ionic groups strongly affects the polymer thermal, mechanical and rheological properties.

Telechelic ionomers provide the opportunity for electrostatic interactions without a deleterious effect on the symmetry of the repeating unit [22]. Moreover, the ionic aggregation occurs only at the ends of the chains, giving rise to an electrostatic chain extension while random ionomers give rise to a gel-like or cross linked aggregation [18]. For this reason, lower melt viscosities and therefore high molecular weights can be obtained for telechelic ionomers with respect to random ionomers [23].

The presence of ionic groups at the end of the polymer chain can be useful for other important applications. For example, we have recently reported the synthesis of PBT telechelic sulfonated ionomers [24] and their ability to consistently increase the heat distortion temperature of PBT nanocomposites since the electrostatic interaction with the surface of the clay platelets gives rise to a better dispersion of the clay and to an improved adhesion between the clay and the polymer [25]. Imidazolium cations should in principle provide a better adhesion to the clay surface (negatively charged) compared to anionic ionomers such as sulfonated ionomers.

For all the reasons reported above the preparation of terephthalate polyesters with potential antibacterial properties, good thermal stability and mechanical properties looks very interesting. The imidazolium ionomers can be prepared by addition of hydroxyl functionalized imidazolium salts during the standard polymerization process of terephthalate polyesters. In this paper we report the synthesis of the OH derivatized imidazolium monomers as well as the first synthesis and the characterization of telechelic imidazolium polyester ionomers. We also report the study of the effect of the different types of counterions and of the length of alkyl chains on the thermal stability and on the polymerization process. Moreover, the anti-microbial effectiveness of the synthesized polymers was evaluated and compared to Triclosan, a widely used antibacterial agent whose safety is, however, not yet fully elucidated.

2. Experimental

2.1. Materials

Potassium hydroxide, imidazole, sodium *p*-toluenesulfonate, 1-bromohexadecane, 6-chlorohexanol, 1,4-butanediol, dimethyl terephthalate, titanium tetrabutoxide, ammonium tetrafluoroborate, ammonium hexafluorophosphate, potassium perfluorobutanesulfonate, potassium trifluoromethanesulfonate and Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol)) (all from Aldrich Chemicals) were high purity products and were not purified before use. PBT Valox 195 was a gift of Sabic-IP.

2.2. Instrumental

^{1}H NMR spectra were recorded using a Varian Mercury 400 spectrometer (chemical shifts are downfield from TMS), using $CDCl_3$ or a $CF_3COOD/CDCl_3$ mixture (1/4, v/v) as solvent. The spectra have been recorded just after dissolution in order to avoid the esterification reaction of end-groups with trifluoroacetic acid.

Gel permeation chromatography (GPC) analysis was performed using a mixture of chloroform/hexafluoroisopropanol (HFIP) (95/5, v/v) as eluent (elution rate 0.3 mL min^{-1}) on a Agilent1100 Series apparatus equipped with a Agilent PL Gel 5 μ Mini-Mixed-C column and a UV detector. Calibration was performed with polystyrene standards.

Calorimetric measurements have been performed using a Perkin Elmer DSC6 instrument equipped with a liquid sub ambient accessory and calibrated with high purity standards (indium and cyclohexane). Dry nitrogen was used as purge gas. The heating and cooling rate were 20 °C/min. All transitions have been measured after a heating scan to 250 °C and cooling down to room temperature in order to delete previous thermal history.

The thermogravimetric analyses (TGA) were performed using a Perkin Elmer TGA7 apparatus in nitrogen (gas flow: 40 mL min^{-1}) at 10 °C/min heating rate, from 25 °C to 800 °C.

DMTA analyses were performed with a Rheometrics dynamic mechanic thermal analyzer DMTA 3E with a dual cantilever testing geometry. Typical test samples were bars that were injection molded at 275 °C using a Minimax Molder (Custom Scientific Instruments) equipped with a rectangular mold ($30 \times 8 \times 1.6$ mm^3). The testing was done at a frequency of 3 Hz and temperature range was from −50 °C to 150 °C at a rate of 3 °C/min.

Inherent viscosities (IV) were measured at 25 °C with an Ubbelhode viscosimeter using a 0.05 M solution of benzyltriethylammonium chloride in 1,1,2,2-tetrachloroethane/phenol 60/40 wt/wt. The salt was used in order to suppress ionic aggregation between chains which can induce an overestimation of molecular weight.

2.3. Antimicrobial properties

A Gram positive strain, *Staphylococcus aureus* ATCC 6538, and a Gram negative strain, *Escherichia coli* ATCC 25645, were used to evaluate the antimicrobial properties of the polymers. The specimens employed were of the same type used for the DMTA analyses (i.e. containing ionic end groups at 0.6, 1 and 2 mol% and Triclosan at 0.6, 1 and 2 mol%) plus a control specimen not containing any agents. Each strain was grown aerobically in Nutrient Broth (NB, provided by Becton, Dickinson and Company, Maryland, USA) for 18 h at 37 °C. The culture thus obtained was centrifuged at 7000 rpm for 10 min, the pellet was washed in sterile saline (8.5 g NaCl/L) and resuspended in saline in order to obtain a cell suspension of 10^8 CFU mL^{-1}. An agar slurry solution was prepared dissolving 0.3 g agar (Biolife Italia, Milan, Italy) in 100 mL saline; the solution was autoclaved at 121 °C for 30 min, cooled at about 40 °C and inoculated with 1 mL of the prepared cell suspension. The specimens were pre-wetted with sterile saline, placed into a petri dish and 0.25 mL of inoculated agar slurry solution were pipette onto the specimen. The cell layer was lower than 1 mm in depth over the entire specimen surface. The slurry solution was allowed to dry, and then the petri dishes containing the inoculated specimens were placed on a capped box in which a 0.5 mm of water was layered in order to avoid sample drying during incubation. Incubation was performed at room temperature for 24 h. After incubation, the specimen was placed in a Stomacher® Bag (Seward, Worthing, United Kingdom) with 10 mL of saline, vigorously shaken for 3 min in a Stomacher Bag apparatus to allow the complete release of agar slurry from the sample. Serial dilutions of the solution were performed, plated on Plate Count Agar (Biolife) plates which were incubated for 48 h at room temperature. Each specimen was processed in triplicate. The percentage of reduction of viable cells was calculated using the following equation:

$$\%\text{reduction} = (a - b) \times 100/a$$

where a is the number of viable cells in the control specimen and b is the number of viable cells in the specimens containing ionic end groups or triclosan.

2.4. Syntheses

2.4.1. 1-Hexadecylimidazole

Potassium hydroxide (16.83 g, 0.300 mol) was added to a dimethyl sulfoxide (DMSO) solution (500 mL) containing imidazole (13.60 g, 0.200 mol). The mixture was then stirred for 30 min at 70 °C and 1-bromohexadecane (64.12 g, 0.210 mol) was added dropwise under vigorous stirring. After 6 h, the mixture was cooled at room temperature and 100 mL of water were added in order to allow the precipitation of the N-alkylimidazole. The precipitate was filtered and washed with distilled water (2 L). The washing procedure was repeated twice.

The final product was dried in an oven under reduced pressure (yield 95%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm from TMS): 0.88 (t, J = 6.9 Hz, 3H, CH_3), 1.20–1.35 (m, 26H, CH_2), 1.77 (quintet, 2H, J = 7.0 Hz, 2H, CH_2–C_{14} chain), 3.92 (t, J = 7.1 Hz, 2H, N–CH_2–C_{15} chain), 6.90 (s, 1H, CH in imidazolium ring), 7.05 (s, 1H, CH in imidazolium ring), 7.46 (s, 1H, N–CH–N in imidazolium ring).

2.4.2. 1-Hexadecyl -3-(6-hydroxyhexyl)imidazolium chloride

6-chlorohexanol (16.59 g, 0.121 mol) was added dropwise under vigorous stirring to a solution containing 1-hexadecylimidazole (32.25 g, 0.100 mol) dissolved in 25 mL of anhydrous toluene. The solution was stirred for 64 h at reflux temperature. The solvent was then distilled under reduced pressure. The residue was washed twice with 500 mL of ethyl acetate and dried under reduced pressure (yield 95%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm from TMS): 0.88 (t, J = 6.9 Hz, 3H, CH_3), 1.20–1.62 (m, 32H, CH_2), 1.72–2.00 (m, 4H, CH_2), 3.58 (t, J = 6.0 Hz, 2H, CH_2–OH), 4.32 (dd, J_1 = 7.3 Hz, J_2 = 7.5 Hz, 2H, N–CH_2–C_5 chain), 4.39 (t, J = 7.3 Hz, 2H, N–CH_2–C_{15} chain), 7.40 (s, 1H, CH in imidazolium ring), 7.62 (s, 1H, CH in imidazolium ring), 10.39 (s, 1H, N–CH–N in imidazolium ring).

2.4.3. 1-Hexadecyl-3-(6-hydroxyhexyl)imidazolium tosylate salt

1-hexadecyl-3-(6-hydroxyhexyl)imidazolium chloride (23.60 g, 0.0550 mol) was dissolved in dichloromethane (DCM) (350 mL) and added to a solution of sodium *p*-toluenesulfonate (11.21 g, 0.0578 mol) dissolved in water (190 mL) in a separating funnel. The content of the funnel was vigorously shaken for 5 min until no further precipitate was present in the resulting two-phase mixture. This procedure was repeated several times (usually twice) until a silver nitrate test was negative confirming the complete exchange of the chloride counter-ion. The organic layer was separated and the solvent removed under reduced pressure. The yellow solid was washed twice with ethyl acetate. The product was dried under vacuum (yield 95%).

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm from TMS): 0.87 (t, J = 6.9 Hz, 3H, CH_3), 1.12–1.60 (m, 32H, CH_2), 1.79 (m, 2H, CH_2), 1.89 (tt, J_1 = 7.1 Hz, J_2 = 7.3 Hz, 2H, CH_2) 2.33 (s, 3H, CH_3 in tosylate ion), 3.57 (t, J = 6.0 Hz, 2H, CH_2–OH), 4.18 (dd, J_1 = 7.3 Hz, J_2 = 7.7 Hz, 2H, N–CH_2–C_5chain), 4.28 (dd, J_1 = 7.1 Hz, J_2 = 7.5 Hz, 2H, N–CH_2–C_{15} chain), 7.16 (d, J = 7.9 Hz, 2H, aromatic CH in tosylate ion), 7.22 (d, J = 1.6 Hz, 1H, CH in imidazolium ring), 7.38 (d, J = 1.6 Hz, 1H, CH in imidazolium ring), 7.77 (d, J = 8.0 Hz, 2H, aromatic CH in tosylate ion), 9.92 (s, 1H, N–CH–N in imidazolium ring).

The synthesis of the imidazolium salts with other counter-ions was performed with the same procedure using ammonium tetrafluoroborate, ammonium hexafluorophosphate, potassium perfluorobutanesulfonate and potassium trifluoromethanesulfonate.

2.4.4. Telechelic PBT ionomers bearing imidazolium end-groups. Synthesis in glass reactor

A round bottom wide-neck glass reactor (250 mL capacity) was charged with 1,4-butanediol (BD) (48.88 g, 0.543 mol), dimethyl terephthalate (DMT) (75.30 g, 0.388 mol) (BD/DMT ratio 1.4/1) and different amounts of 1-hexadecyl-3-(6-hydroxyhexyl)imidazolium salt depending on the ionic concentration to be obtained. Titanium tetrabutoxide (TBT) (0.106 g, 0.312 mmol, 175 ppm as titanium with respect to the final polymer weight) was introduced into the reactor that was closed with a three-neck flat flange lid equipped with a mechanical stirrer, a torque meter and a heating band at 90 °C. The system was then connected to a water-cooled condenser and immersed in a thermostatic salt bath at 215 °C and the stirrer switched on at 140 rpm. After 2 h, the temperature was increased to 245 °C, the lid was heated at a temperature of 120 °C and the reactor connected to a liquid nitrogen cooled condenser. Dynamic vacuum was then applied to reduce the pressure down to 0.2 mbar in 60 min. After 75 min the very viscous and transparent melt was discharged from the reactor.

2.4.5. Telechelic PBT ionomers bearing imidazolium end-groups scale-up polymerization

Micro-pilot plant polymerizations were carried out by using a two-stage process in a 1.8 L stainless steel batch reactor equipped with a paddle stirrer (driven at 60 rpm) and a strain-gauge sensor mounted on the stirrer shaft in order to monitor the viscosity of the reaction melt (and indirectly the increase of PBT molecular weight) during the polymerization. Two condensers in series (the first water-cooled and the second liquid nitrogen-cooled) were connected to the reactor to collect volatile products during the first and second stages. A typical polymerization procedure is described below.

2.4.5.1. First stage. BD (742.0 g, 8.25 mol), DMT (800.0 g, 4.12 mol) and 1-hexadecyl-3-(6-hydroxyhexyl) imidazolium tosylate salt (in different amounts in order to insert ionic groups at a content 0.6, 1 and 2 mol% respect to DMT) were loaded into the reactor and then heated at atmospheric pressure under stirring to 180 °C. At this temperature, titanium butoxide (1.13 g, 3.31 mmol, 175 ppm as titanium with respect to the final polymer weight) was introduced into the reactor. The reaction temperature was increased from 180 to 215 °C. Volatile products (methanol and THF) were distilled off from the reactor, condensed in the water-cooled condenser and collected in a graduated cylinder. The start of the first stage was taken when the first drop of liquid was collected in the water-cooled condenser. The temperature was then kept at 215 °C until 95% of the theoretical amount of methanol was distilled off. The distilled volume was recorded versus time as an indicator of the catalytic activity during the first stage and distillate samples were analyzed by ^{1}H NMR in order to measure the methanol/THF ratio and thus the rate of THF formation.

2.4.5.2. Second stage. The internal pressure was slowly reduced, first from atmospheric pressure down to 10 mbar in 30 min, then from 10 mbar to 1 mbar in 20 min. At the same time the temperature of the reaction melt was increased to 240 °C and kept at this temperature until the end of the polymerization. The start of second stage was taken when the minimum pressure was reached. The second stage was stopped when no further significant increase in strain gauge signal was detected.

3. Results and discussion

3.1. Monomers synthesis and small scale polymerization

Imidazolium salts need to be modified in order to be inserted at the end of the polyester chain. The approach we have followed consists in the derivatization of the imidazolium ring with an alkyl chain bearing an OH group that can react with the methyl ester group of DMT and of the growing polymer chain during the poly-

condensation process. Moreover, we have decided to insert a hexadecyl alkyl chain on the imidazolium ring in order to impart antimicrobial properties to the polyester ionomer (Fig. 1).

The imidazolium salts bearing one long alkyl chain and an OH group have been prepared from imidazole using a novel synthetic route (Fig. 2) that consist in the insertion of the first alkyl chain followed by the insertion of the hydroxyalkyl chain and then by the exchange reaction of the chloride ion with the desired counterion. The synthetic method is versatile and allows the preparation of a wide range of products with different alkyl chain length and different counterions.

As reported in the literature [17] chloride and bromide salts are not stable enough to sustain the polymerization and processing conditions for terephthalate polyesters since they start degrading below 240 °C. On the other hand, tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), perfluorobutanesulfonate ($C_4F_9SO_3^-$), trifluoromethanesulfonate ($CF_3SO_3^-$) and tosylate (TsO^-) salts, that can be prepared by the counterion exchange procedure described in step 3 in Fig. 2, are stable at temperatures up to 260 °C, as reported in the TGA curves in Fig. 3.

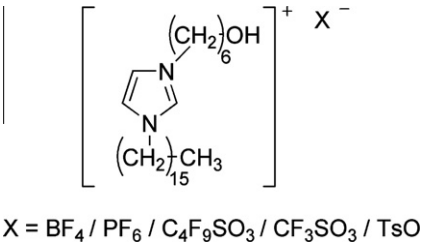

Fig. 1. Hydroxy-derivatized imidazolium salts with long alkyl chain.

Imidazolium salts with $C_4F_9SO_3^-$ and $CF_3SO_3^-$ counterions are the most stable followed by TsO^-. An incomplete exchange of Cl^- or Br^- ions for more stable counterions is detrimental for the thermal stability of imidazolium salts and can be revealed by multiple weight loss steps in TGA curves. For this reason, the exchange method has been improved with respect to those reported in the literature [17]. Indeed, an incomplete exchange was observed (by TGA) using CH_3CN as solvents while using a two-phase H_2O/CH_2Cl_2 mixture, the complete exchange was obtained.

The imidazolium salts have been added along with the other monomers at the beginning of the polymerization of poly(butylene terephthalate) as reported in the scheme in Fig. 4.

The first set of experiments was conducted in small-scale glass reactors in order to identify the type of counterion having the right properties required to reach high molecular weight polymers. A study was performed in order to evaluate the effect of imidazolium salts on the polymerization rate during the first stage. The reaction rate was monitored by measuring the amount of methanol distilled during the first stage. The curves in Fig. 5 show the dramatic effect of different counterions on catalyst deactivation. In particular $C_4F_9SO_3^-$, PF_6^- and BF_4^- completely inhibits the catalyst and only low molecular weight oligomers were produced. Tosylate salts present the optimal combination of properties in terms of high thermal stability and low deactivation of TBT catalyst. Indeed, with this counterion it was possible to obtain telechelic imidazolium polyesters using the normal polycondensation conditions for PBT (i.e. 1.4 BD/DMT ratio, 175 ppm of TBT as catalyst and 2 h of first and second stage). Moreover, the amount of THF formed was comparable with that recorded in a normal PBT polymerization. The color of PBT ionomers made using tosylate salts was good since almost no discoloration was observed while for the other salts dark colored materials were obtained.

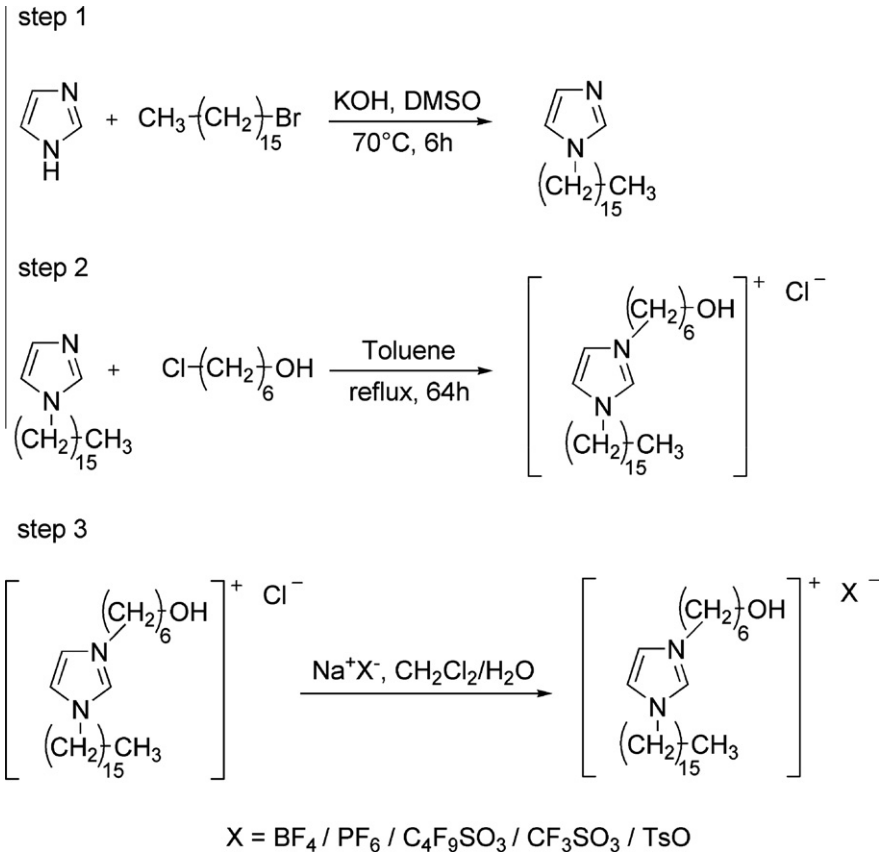

Fig. 2. Synthesis of imidazolium salts bearing hydroxyalkyl groups.

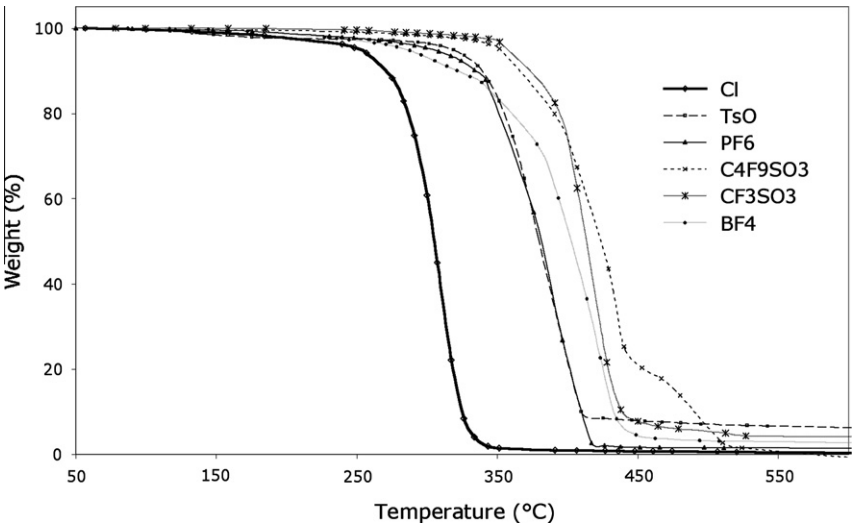

Fig. 3. Thermal stability of 1-hexadecyl-3-(6-hydroxyhexyl)imidazolium salts.

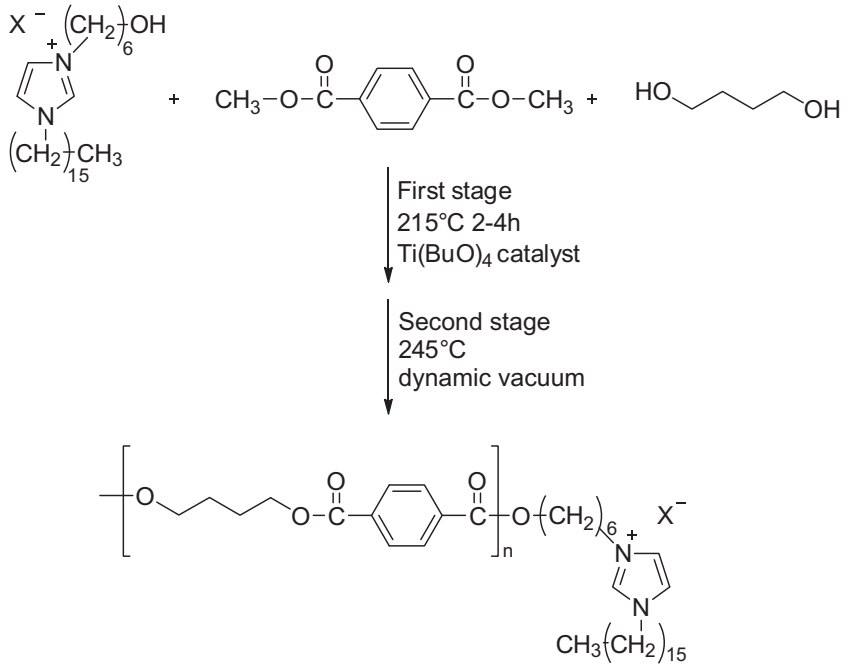

Fig. 4. Polymerization scheme of PBT imidazolium telechelic ionomers.

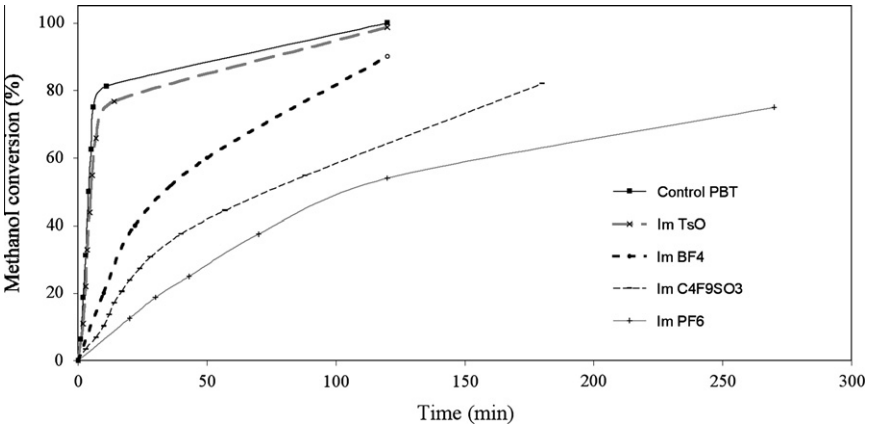

Fig. 5. First stage conversion using different counterions and Titanium catalysts.

Table 1
End-groups and molecular weight of ionomers obtaining using 2% of imidazolium salts compared with commercial PBT VALOX 195.

Sample	CH_2OH end-groups (%)[a]	Methyl ester end-groups (%)[a]	Ionic end-groups (%)[a]	NMR[b] M_n	GPC[c] M_n	GPC PDI[d]
Commercial PBT	1.61	0.08	/	26,300	24,900	2.4
Im-TsO	0.02	0.03	1.91	22,100	26,000	2.8
Im-BF_4	/	0.41	2.00	18,300	11,100	3.8
Im-$C_4F_9SO_3$	1.32	6.30	1.82	4600	2000	2.8

[a] Mol% respect to terephthalate units in PBT.
[b] Molecular weight calculated using end-groups measured by ^{1}H NMR spectroscopy.
[c] Molecular weight calculated using GPC.
[d] Polydispersity index measured by GPC.

The results of the molecular characterization of different PBT telechelic imidazolium ionomers containing 2 mol% of imidazolium groups bearing a hexadecyl alkyl chain and a $-(CH_2)_6OH$ group is reported in Table 1.

Using the TsO^- imidazolium salt a low level of both methylester and OH end-groups has been obtained while using the imidazolium BF_4^- salt only methylester groups were present in large amounts. Therefore, in this second case the molecular weight was limited since methylester groups were not able to react anymore due to the complete consumption of hydroxyl end-groups. Moreover, using BF_4 salts the M_n calculated by GPC was lower respect to the M_n measured by end-group analysis by NMR since this second method does not take into account the COOH end-groups formed by degradation reactions. Using the BF_4 salt a longer reaction time was needed in order to obtain a sufficiently high methanol conversion to apply vacuum in the second stage and therefore a more consistent COOH end-groups formation must be expected. The use of the $C_4F_9SO_3^-$ salt produces only oligomers with a consistent amount of methylester end-groups due to very strong inhibiting effect of the salt on the titanium based catalyst. No vinyl end-groups were detected by ^{1}H NMR.

The ^{1}H NMR spectra of the imidazolium salt and of the 2% telechelic ionomer after dissolution in $CHCl_3/CF_3COOH$ (4/1, v/v) and precipitation in methanol are reported in Fig. 6.

The presence of the signals of the imidazolium group after the precipitation in methanol (that is a solvent for the imidazolium salt) confirms that the ionic groups are covalently bonded to the polymer backbone. The amount of imidazolium salt was calculated comparing the signal at δ 8.58 ppm (1H of imidazolium salt) with the signal at δ 8.15 ppm (4H of the terephthalate group). OH end-groups were measured using the peak at δ 3.90 ppm (2H) while the methylester end-groups using the singlet at 4.05 ppm (3H). The ^{1}H NMR spectrum also shows that no significant side-reactions takes place during the synthesis, as the peaks in the spectrum are those expected from the structure of the imidazolium salt added.

A second set of experiments in small-scale glass reactors was performed in order to define the optimal length of the two alkyl chains bonded to the imidazolium ring. Using a chain spacer consisting of two methylene units between the OH and the imidazolium ring, only a small amount (below 10%) of imidazolium groups was bonded to the polymer chain ends (as detected by ^{1}H NMR after dissolution in $CHCl_3/CF_3COOH$ (4/1, v/v) and precipitation in methanol). The low incorporation yield of the imidazolium ionic groups was attributed to the lower reactivity of the $-C_2H_4OH$ group compared to longer alkyl chain spacers. Indeed, using a longer spacer, with 6 methylene units, an almost complete insertion of imidazolium groups at the end of the polymer chain was achieved. Also the length of the non-reactive alkyl chain has an important effect on the polymerization process. In particular, we have observed that when imidazolium salts with short alkyl chains were used, the polydispersity index was high. For example a polydispersity index of 10 was obtained with an alkyl chain with two carbon atoms. On the contrary, using longer (hexadecyl) alkyl chains, a polydispersity index below 3 was achieved. This behavior was attributed to the increased solubility in the reaction mixture of the imidazolium salt with the long alkyl chain. Moreover, the imidazolium groups with hexadecyl alkyl chain are also the most interesting in view of the use of these ionomers for antimicrobial applications [8].

For all the reasons reported above, an imidazolium TsO^- salt bearing a hexadecyl chain and a $-(CH_2)_6OH$ group has been used in the scale-up of the experiments in the micro pilot-plant.

3.2. Scale-up in micro pilot-plant

The polymerization process using the imidazolium tosylate salt at 0.6 (Im-TsO-0.6), 1 (Im-TsO-1), and 2 mol% (Im-TsO-2), was then scaled-up in the 1.8 L micro pilot-plant in order to measure the THF formation and prepare larger amounts of polymers for further characterization. The final polymer melt was completely transparent and clear becoming white after crystallization. No discoloration, presence of solid impurities or side-reactions were observed.

No significant catalyst deactivation was observed following first stage conversion versus time (Fig. 7) by measuring the amount of methanol distilled during the first stage in the water-cooled condenser.

The results of the polymerization are reported in table 2. Benzyltriethylammonium chloride was added to the solvent for inherent viscosity (IV) measurements in order to increase the ionic strength of the solution and therefore decrease ionic aggregations between the chain ends [26].

GPC results have to be considered with special care since in the case of ionomers there is the possibility for ionic aggregation between the end of chains and for electrostatic interactions with the column walls. These effects may explain why the molecular weight values calculated by GPC are higher for the PBT ionomers with 0.6% of end-groups compared to the normal PBT. This is in contrast with end-groups analysis that shows comparable amounts of methyl ester and OH groups. Also COOH end-groups content should be higher for ionomers due to side-reactions. The higher amount of side-reactions is confirmed by the analysis of THF amount formed by side-reactions due to the catalytic effect of imidazolium groups. Therefore, on the basis of end-groups analysis, the molecular weight should be lower for PBT ionomers due to the higher content of end-groups (OH, methyl ester, carboxylic and ionic).

IV analysis, on the contrary with respect to GPC measurements, shows a correlation between ionic content and molecular weight. Inherent viscosity decreases as expected by increasing the ionic content, since the imidazolium groups act as end-cappers. Nevertheless, the molecular weight of the ionomers prepared is sufficiently high for several PBT applications.

Thermal properties were investigated by TGA in order to assess the effect of imidazolium end-groups on the thermal stability of PBT ionomers. In Table 3 T_{ONSET} (the temperature at which the weight loss in the TGA curve begins), and T_D (the temperature at which the weight loss takes place at the highest rate) are reported.

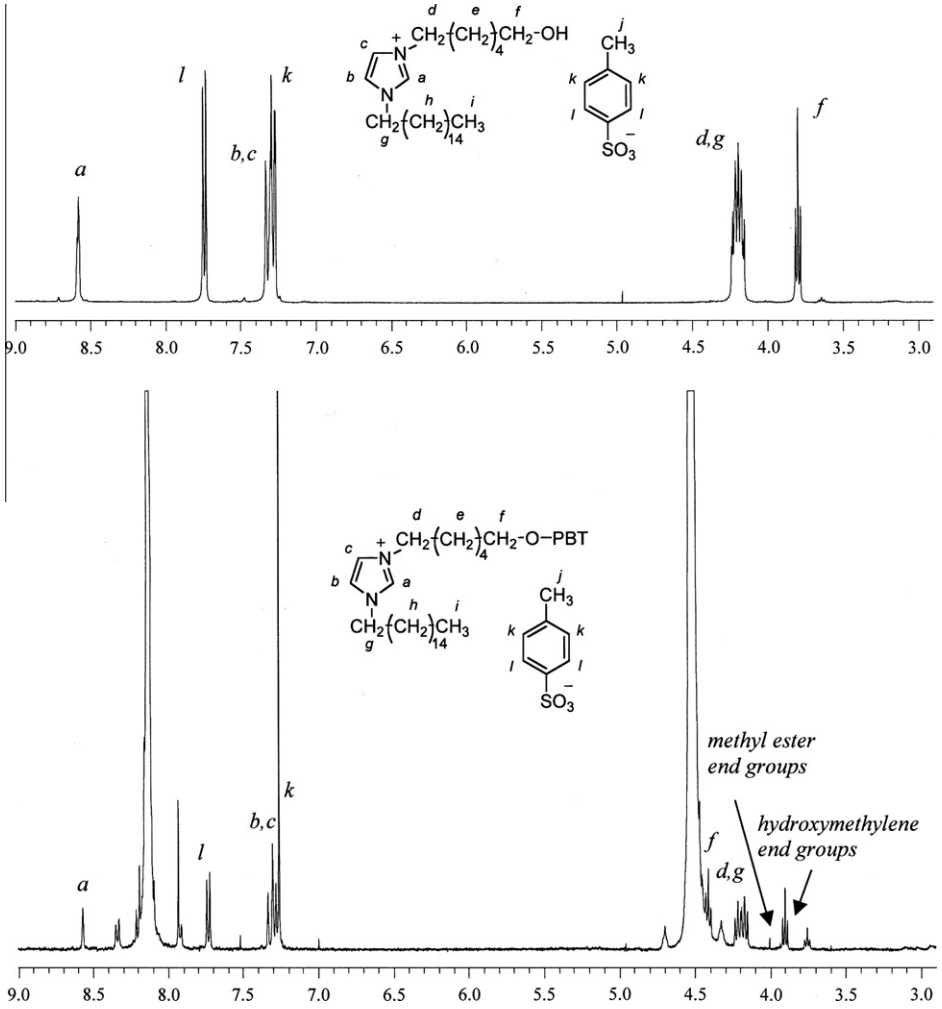

Fig. 6. ^{1}H NMR of the OH derivatized TsO^- imidazolium salt (A) and of the ionomer with 2% TsO^- imidazolium after dissolution in $CHCl_3/CF_3COOH$ (4/1) and precipitation in methanol (B).

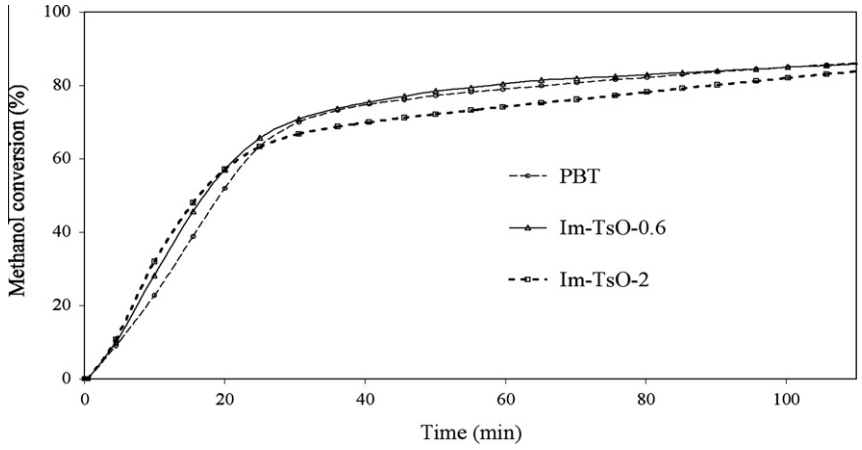

Fig. 7. Conversion during the first stage of PBT synthesis starting from DMT, BD and different amounts of Im-TsO.

From the results obtained, the ionic end-groups have a limited detrimental effect on thermal stability. Indeed, a maximum decrease of 20–24 °C was observed for the ionomer with 2.0 mol% imidazolium tosylate salt. However, the thermal initial degradation temperature of all the ionomers is well above the typical processing temperature of PBT. The DSC results show that both the melting temperature and the crystallinity are comparable with those of standard PBT while the crystallization rate is slightly higher since in the cooling scan the T_{cc} is about 4 °C higher, indicating that the ionic polymers crystallize faster probably due to the lower M_w or to chemical nucleation effects caused by ionic end-groups [27].

Table 2
polymerization scale-up results.

Sample	THF in 1st stage (%)[a]	Methylester end-groups (%)[b]	CH_2OH end-groups (%)[b]	Ionic end-groups (%)[b]	M_n NMR[c]	M_n GPC[d]	PDI[e] GPC	Inherent Viscosity (dL/g)
PBT control	1.80	0.52	1.02	–	28,570	29,800	2.5	0.79
Im-TsO-0.6	3.49	0.54	0.98	0.60	20,750	39,400	2.9	0.77
Im-TsO-1	6.35	0.31	0.86	1.01	20,100	28,900	2.8	0.71
Im-TsO-2	9.57	0.35	0.98	2.00	13,200	27,800	2.9	0.60

[a] Mol% respect to BD in the feed.
[b] Mol% respect to terephthalate units in PBT.
[c] Molecular weight calculated using end-groups measured by ^{1}H NMR spectroscopy.
[d] Molecular weight calculated using GPC.
[e] Polydispersity index measured by GPC.

Table 3
Thermal properties of the PBT ionomers prepared in the scale-up polymerization.

Sample	T_D (°C)	T_{ONSET} (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)
PBT control	424	398	176	−48.0	220	37.9
Im-TsO-0.6	414	388	177	−51.6	221	32.6
Im-TsO-1	420	393	176	−49.7	221	39.6
Im-TsO-2	401	374	180	−52.1	221	44.0

T_D = temperature of the maximum degradation rate, measured in TGA under N_2 flow at 10 °C/min.
T_{ONSET} = temperature of the beginning of degradation by TGA weight loss.
T_{cc} = crystallization temperature measured in DSC during the cooling scan at 20 °C/min.
ΔH_{cc} = enthalpy of crystallization.
T_m = melting temperature measured in DSC during the 2nd heating scan at 20 °C/min.
ΔH_m = enthalpy of fusion.

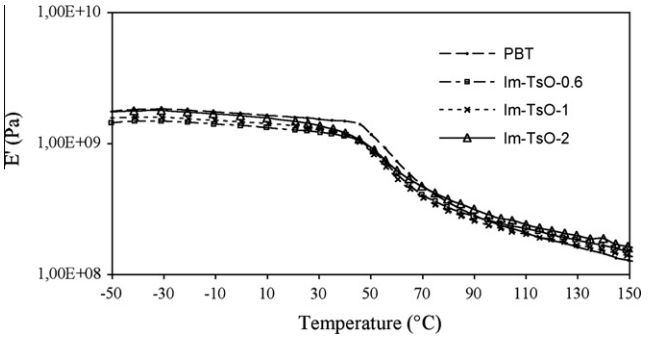

Fig. 8. Storage modulus measured by DMTA analysis.

DMTA analysis (Fig. 8) shows that ionomers present a lower modulus below T_g but a slightly higher modulus above glass transition temperature. However, a correlation between ionic group content and thermo-mechanical properties has not been found. T_g of ionomers measured by DMTA is always comparable with that of standard PBT.

3.3. Antimicrobial properties

In order to demonstrate the anti-bacterial effectiveness of the imidazolium telechelic based polymers, specimens containing imidazolium ionic end groups at different concentrations and control specimens were placed in contact with cells of *S. aureus*, a Gram positive bacterium, and *E. coli*, a Gram negative one. The viability of the bacteria present on the surface was evaluated and the percentage of reduction of viable cells in the treated specimens with respect to controls was calculated. PBT containing Triclosan was also tested in order to compare the behavior of telechelic ionomers with a commercially available AM product. Triclosan was blended with PBT at different concentration in a Brabender Plasticorder mixer obtaining a pale brown material. The results are presented in Table 4.

Table 4
Percentage of reduction of viable *S. aureus* and *E. coli* cells in the treated specimens compared to the control specimens.

Sample (%)	Reduction of viable cells (%)[a]	
	Staphylococcus aureus	*Escherichia coli*
Ionic end groups 0.60	89.4 ± 5.7	26.3 ± 2.9
Ionic end groups 1.00	75.0 ± 6.8	24.5 ± 3.2
Ionic end groups 2.00	97.5 ± 6.4	48.5 ± 5.4
Triclosan 0.60	83.5 ± 3.6	42.9 ± 3.8
Triclosan 1.00	91.2 ± 3.0	75.5 ± 5.4
Triclosan 2.00	99.4 ± 2.7	74.6 ± 2.3

[a] Calculated as follows: % reduction = $(a - b) \times 100/a$, where a is the number of viable cells in the control specimen and b is the number of viable cells in the treated specimens.

The results obtained clearly evidence the high anti-bacterial effectiveness of the imidazolium telechelic based polymers on Gram positive bacteria, which is comparable to that of Triclosan containing specimen. The biological activity of the imidazolium polymers against *E. coli*, although lower with respect to Triclosan, is of great interest considering that, generally, Gram negative strains are less susceptible to antimicrobial agents, including imidazolium salts [28].

4. Conclusions

We have synthesized for the first time imidazolium telechelic terephthalate polyesters by adding an imidazolium tosylate salt bearing a long alkyl chain and a hydroxyl group. The ionic groups were bonded to PBT chains as end-groups in high yield and they did not affect properties like color and thermal stability. Using a tosylate salt no catalyst deactivation has been observed and a normal polymerization procedure and a standard catalyst loading can be used. This method can be used for the preparation of imidazolium telechelic ionomers of other polycondensation polymers (e.g. aliphatic polyesters, polycarbonates and copolymers). The imidazolium ionomers have proved to be very active against *S. aureus* even at low concentration (0.6 mol%) while a lower activity has been observed against *E. coli*.

Acknowledgement

This work was financed by SABIC-IP.

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