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Synthesis and characterization of sulfonated telechelic bisphenol A polycarbonate ionomers

Martino Colonna [a,*], Corrado Berti [a], Enrico Binassi [a], Maurizio Fiorini [a], Simone Sullalti [a], Francesco Acquasanta [a], Sreepadaraj Karanam [b], Daniel J. Brunelle [c]

[a] Dipartimento di Ingegneria Civile, Ambientale e dei Materiali, Via Terracini 28, 40131 Bologna, Italy
[b] SABIC Innovative Plastics, Plasticslaan 1, 4600 AC Bergen op Zoom, The Netherlands
[c] General Electric Global Research, One Research Circle, Niskayuna, NY 12309, United States

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ABSTRACT

Bisphenol A polycarbonate telechelic sulfonated ionomers have been prepared by melt polycondensation using bis(methyl salicyl) carbonate (BMSC), bisphenol A (BPA) and the sodium salt of sulfobenzoic acid phenylester (SBENa). Using an activated carbonate such as BMSC it is possible to decrease both reaction temperature and time respect to a standard polycondensation that use diphenylcarbonate (DPC) as carbonate precursor. Using the activated carbonate, ionomers with low Fries by-products and with good color have been obtained. The addition of SBENa permits the preparation of telechelic ionomers with ionic contents up to 3 mol%. All the properties of the telechelic ionomer obtained using BMSC are superior respect to those of the telechelic ionomers obtained using DPC. In particular, the ionomers prepared using BMSC are stable up to 400 °C and present higher glass transition temperature and storage modulus respect to standard PC.

1. Introduction

The presence of covalently bonded ionic groups along the polymer chain produces a consistent modification on the physical and rheological properties of polymers [1–4]. Indeed, ionomers (polymers containing less than 10 mol% of ionic groups) have been shown to exhibit considerably higher moduli and higher glass transition temperatures compared to those of their non-ionic analogues [1]. Improvements in mechanical and thermal performance are generally attributed to the formation of ionic aggregates, which act as thermo-reversible cross-links [1] and effectively retard the translational mobility of polymeric chains. The thermo-reversible nature of ionic aggregation may address many other disadvantages associated with covalently bonded high molecular weight polymers, such as poor melt processability, high melt viscosity and low thermal stability at typical processing conditions such as high shear rate and temperature.

Telechelic ionomers are polymers with ionic groups selectively located at the end of the polymer chains that provide the opportunity for electrostatic interactions without a deleterious effect on the symmetry of the repeating unit [5]. Moreover, the ionic aggregations occur only at the end of the chain, giving rise to electrostatic chain extension. On the contrary, random ionomers (polymers with ionic groups randomly distributed along the polymer chain) give rise to a gel-like or cross-linked aggregation [1]. For this reason, telechelic ionomers having lower melt viscosities and higher molecular weights than random ionomers can be prepared [6]. We have reported [7,8] the synthesis of telechelic poly(butylene terephthalate) (PBT) ionomers and a comparison with PBT random ionomers. We have observed higher thermal and hydrolytic stability and lower melt viscosity for telechelic ionomers respect to random ionomers.

We have also reported [9,10] the positive effect of ionic groups in PBT/montmorillonite nanocomposites. Indeed, nanocomposites prepared with PBT telechelic ionomers present a better dispersion of the organo-modified clay and better thermo-mechanical properties (higher heat distortion temperatures and modulus) respect to the nanocomposite of non-ionic polymers.

On the basis of our work on polyester ionomers we have extended our studies to bisphenol A polycarbonates (PC). The presence of ionic groups should improve the clay dispersion in PC/clay nanocomposites and should, in principle, also consistently change the rheological properties of BPA polycarbonates. To the best of our knowledge only one patent reports the synthesis of PC telechelic sulfonated ionomers [11]. The authors report that PC ionomers, prepared by melt and interfacial methods, present a strong non-Newtonian melt rheology behavior along with increased solvent and flame resistance. However, they do not present any direct evidence of the insertion of ionic groups in the polymer

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* Corresponding author. Fax: +39 0512090322.
E-mail address: martino.colonna@unibo.it (M. Colonna).

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chain and no complete chemical characterization is provided. Moreover, it is well known that ionic groups and sodium salts catalyze degradation reaction in PC [12]. Therefore, high degradation rates should be expected in the melt polycondensation synthesis of ionomeric sulfonated PC due to the high reaction temperature (280–300 °C) and long residence time required to achieve high molecular weight polymers. The reason of the choice of positioning the ionic groups selectively as end-groups is related to the high melt viscosity of polycarbonate. The presence of ionic groups increases the melt viscosity and therefore the elimination of the low molecular product, necessary to increase molecular weight, becomes more difficult. It is well known that random ionomers give rise to cross-link type aggregations while telechelic ionomers produce chain-extension type aggregations. Therefore, a consistently higher melt viscosity is expected for random ionomers with respect to telechelic ionomers with the same amount of ionic moieties.

Activated carbonates, such as bis(methyl salicyl) carbonate (BMSC) can be used in order to decrease polymer degradation [13,14]. The use of this more active carbonate allows a shorter polycondensation process at lower temperatures (270 °C) [13,14]. Moreover, the equilibrium of the reaction between BPA and BMSC is shifted toward the formation of the products (94%) and therefore the reaction proceeds even without the continuous elimination of the reaction products while using DPC the reaction equilibrium is shifted towards the reagents and the continuous elimination of phenol is necessary to reach high conversion and high molecular weights [15]. For these reasons the use of BMSC must be preferred when long reaction time and high temperature must be avoided in order to decrease side reactions.

In this paper we report the first synthesis and characterization of bisphenol A polycarbonate ionomers using activated carbonates by a melt polycondensation process.

2. Experimental

2.1. Materials

Sodium 3-sulfobenzoic acid, diphenyl carbonate, sodium carbonate, bisphenol A, tetramethylammonium hydroxide, sodium hydroxide (all from Aldrich Chemicals) were high purity products and were not purified before use. Bis(methyl salicyl) carbonate was a gift from SABIC-IP [13].

2.2. Synthesis

2.2.1. Preparation of phenyl 3-sulfobenzoate sodium salt (SBENa)

A 1 L, 3-neck flask equipped with thermometer, mechanical stirrer and distillation head was filled with sodium 3-sulfobenzoic acid (133.3 g; 0.67 mol), diphenyl carbonate (288.0 g; 1.34 mol) and sodium carbonate (1.500 g; 14.0 mmol). The flask was placed under a nitrogen atmosphere and heated with a heating mantle. Once the diphenyl carbonate was melted the mechanical stirring was started. When the temperature of the melt reached 300 °C phenol started to distill. After about 30 min phenol distillation stopped and the heat was removed. The dark melt solidified to a yellow solid. After cooling the solid was removed from the flask and dissolved in approximately 400 mL of water. The aqueous solution was washed twice with 300 mL of methylene chloride and then the water was removed by rotary evaporation to yield the crude product. The solid was then suspended in ethanol and warmed on a steam bath to form a solution. The solution was hot filtered and then heated on the steam bath to evaporate the solvent until the beginning of the crystallization. The solution was cooled to room temperature and then put in a refrigerator at about 5 °C. The product was collected by filtration and dried in a vacuum oven at 90 °C and characterized by ^{1}H NMR analysis and melting temperature (287 °C).

2.2.2. Preparation of sulfonated telechelic PC using BMSC

A round bottom wide-neck glass reactor (250 mL capacity) was charged with bisphenol A (25.30 g; 110.8 mmol), SBENa (1.00 g; 3.32 mmol) and the catalyst water solution (a mixture of 2.22×10^{-2} mmol tetramethylammonium hydroxide and 8.43×10^{-5} mmol of NaOH in 0.1 mL of H_2O).

The reactor was closed with a three-neck flat flange lid equipped with a mechanical stirrer, a torque meter, a nitrogen inlet and the system was then connected to a liquid nitrogen cooled condenser. The reactor was purged three times with nitrogen and immersed in a thermostated molten salt bath at 210 °C and the stirrer switched on at 100 rpm after complete melting of the reactants. After 90 min BMSC (36.95 g; 111.9 mmol) was carefully added and dynamic vacuum was applied at 130 mbar for 10 min. The temperature was then increased to 260 °C in 10 min and the pressure decreased to 1 mbar. The reaction melt was very viscous after 10 min from the application of dynamic vacuum and the stirring was very difficult and slow in the last part of the polymerization. After 30 min from the application of the vacuum, the very viscous pale yellow and transparent melt was discharged from the reactor.

2.2.3. Preparation of sulfonated telechelic PC using DPC

The reactor was filled with diphenyl carbonate (11.08 g, 0.52 mol) bisphenol A (11.25 g, 0.49 mol) and sodium phenyl 3-sulfobenzoate. The reactor was heated to 220 °C under a nitrogen atmosphere. The catalyst (an aqueous mixture of 2.22×10^{-2} mmol tetramethylammonium hydroxide and 8.43×10^{-5} mmol of NaOH in 0.1 mL of H_2O) was added to the stirred reaction solution. The reaction pressure was then reduced at 30 mbar/min down to 30 mbar and then at 5 mbar/min until a final pressure of 0.2 mbar was reached. The reaction temperature was increased to 280 °C and maintained at that temperature for 2 h at full vacuum. The viscous brown melt was then discharged from the reactor.

2.3. Physico-chemical characterization

^{1}H NMR spectra were recorded with a Varian XL-400 spectrometer (chemical shifts are downfield from TMS), using hot deuterated DMSO as solvent. The spectra have been recorded just after dissolution in order to avoid the precipitation of the polymer.

Gel permeation chromatography (GPC) analysis was performed using chloroform as eluent (elution rate of 0.3 mL/min) on a HP 1100 Series apparatus equipped with a PL Gel 5 μ Mini-Mixed-C column and a UV detector. Calibration was performed with polystyrene standards. Benzyltriethylammonium chloride (0.05 mol/L) was also added in order to suppress ionic aggregations.

Differential scanning calorimetry (DSC) analysis was performed using a Perkin Elmer DSC6. The instrument was calibrated with high purity standards (indium and cyclohexane). Dry nitrogen was used as purge gas. DSC heating and cooling rates were 20 °C/min. All transitions have been measured after a heating to 270 °C and cooling to room temperature in order to delete previous thermal history.

The thermogravimetric analyses (TGA) were performed using a Perkin Elmer TGA7 apparatus in N_2 (gas flow: 40 mL/min) at 10 °C/min heating rate, from 60 °C to 800 °C.

Dynamical mechanical thermal (DMTA) analyses were performed with a Rheometrics dynamic mechanic thermal analyzer DMTA 3E with a single cantilever testing geometry. Typical test samples were bars that were compression molded at 260 °C. The testing was done at a frequency of 3 Hz and temperature range was from −50 °C to 200 °C at a rate of 3 °C/min.

Melt rheologic properties were measured by a stress-controlled Rheometric Scientific SR5 rheometer using a parallel plate geometry with a disc diameter of 25 mm. The frequency was varied from 0.1 rad/s to 500 rad/s. Typical test disk specimens were compression molded at 260 °C using a Carver press and a custom made mold.

3. Results and discussion

The method reported in literature [11] for the melt polycondensation synthesis of telechelic sulfonated PC consists in the addition of the phenylester of sulfobenzoic acid sodium salt (SBENa) at the beginning of the polycondensation between bisphenol A (BPA) and diphenylcarbonate. However, when we performed this method we obtained a consistent amount of degradation products obtaining a dark yellow material not completely soluble in dichloromethane. The main reason of this insolubility can be ascribed to the cross-linking due to the formation of Fries rearrangement by-products caused by the catalytic effect of the ionic groups towards side reactions. Therefore, in order to decrease the amount of side-product an activated carbonate (such as BMSC) must be used.

The one-pot reaction of BMSC, BPA and SBENa does not produce telechelic ionomers since the reaction mixture remains opaque and the SBENa can be mainly recovered unreacted at the end of the polymerization process. In order to improve the reaction of BMSC with BPA we have adopted an approach similar to that used for telechelic PBT synthesis [8]. This method (Fig. 1) consists in pre-reacting the sulfobenzoic acid derivative with the diol (in this case BPA) in order to improve the solubility of the salt. Moreover, ^{1}H NMR analysis of samples taken during the first stage of polymerization shows that the reaction of BMSC and BPA is consistently faster than the reaction of SBENa with BPA. Therefore, after a few minutes of reaction the amount of unreacted BPA drops consistently thus decreasing the reaction rate with SBENa. The pre-stage was conducted for 90 min at 210 °C. The ^{1}H NMR analysis (Fig. 2) shows the almost complete reaction of the SBENa with BPA. BMSC was then added and the vacuum was slowly reduced to 130 mbar. The temperature was then increased to 260 °C while the vacuum decreased to 0.1 mbar. The reaction melt became very viscous in a few minutes and the reaction was carried at full vacuum for additional 30–45 min. A pale yellow and completely transparent polymer was obtained. The excess of BMSC used depends on the reactor geometry. However, the stoichiometry can be easily balanced by measuring by ^{1}H NMR the amount of end groups deriving from BPA or BMSC.

The ^{1}H NMR spectra of samples taken during the pre-stage (Fig. 2) show that the progress of the reaction between SBENa and BPA can be followed by comparing the two peaks at δ8.64 and 8.68 ppm ascribable to the reacted and unreacted sulfobenzoic acid phenylester, respectively. After 90 min at 210 °C most of the SBENa has already reacted. The ^{1}H NMR analysis have been conducted in deuterated DMSO since using this solvent it was possible to obtain spectra with signals more separated and therefore easier to integrate in order to measure the ionic content respect to the use of $CDCl_3$ as solvent.

The ^{1}H NMR spectrum of the crude product (Fig. 3) shows that no unreacted SBENa is left and that no side-reaction take place using BMSC as monomer. We have not observed any significant evidence of the reaction of the methyl ester group of BMSC with SBENa or BPA. Moreover, no singlet at δ8.15 ppm due to Fries by products is present [16]. On the contrary using DPC a consistent amount of Fries products was present in the fraction soluble in hot deuterated DMSO. In this case the final polymer was not completely soluble both in hot DMSO and in chloroform indicating that part of the polymer has been cross-linked by side reactions such as Fries rearrangements. Due to this not complete solubility we have not measured the molecular weight of PC telechelic ionomers made from DPC.

The TGA analysis (Fig. 4) shows that the 3 mol% telechelic ionomer prepared using BMSC is consistently more stable (30 °C) compared to that prepared from DPC. Moreover, the telechelic PC from DPC is consistently darker. The stronger degradation and side reactions that occurs using DPC can be ascribed to the longer reaction times and temperature needed for the synthesis without the activated carbonate.

The molecular weight, thermal properties and end-groups are reported in Table 1. The amount of ionic end groups have been calculated comparing the signal at 8.7 ppm (1H form the ionic end-groups) with the integral of the signals between 7.4 and 7.1 ppm (8H of BPA group). OH end groups have been calculated comparing the signal at 6.6 ppm (2H of aromatic protons close to OH) with total BPA signals (7.4–7.1 ppm). For methyl salycilate end groups we have compared the signal at 8.12 ppm (1H of methyl salycilate) with total BPA signals (7.4–7.1 ppm). The molecular weight calculated by end-groups analysis (by ^{1}H NMR) shows a good correlation with ionic content since ionic groups act as chain stoppers and therefore the molecular weight should decrease increasing the ionic content. On the contrary, an opposite trend has been found when molecular weight was measured by GPC in chloroform as solvent. This behavior can be explained by the ionic aggregation that produces polymer–polymer and polymer–column interactions. In order to suppress ionic interactions, benzyltriethylammonium chloride was added since it is reported in the literature [17]

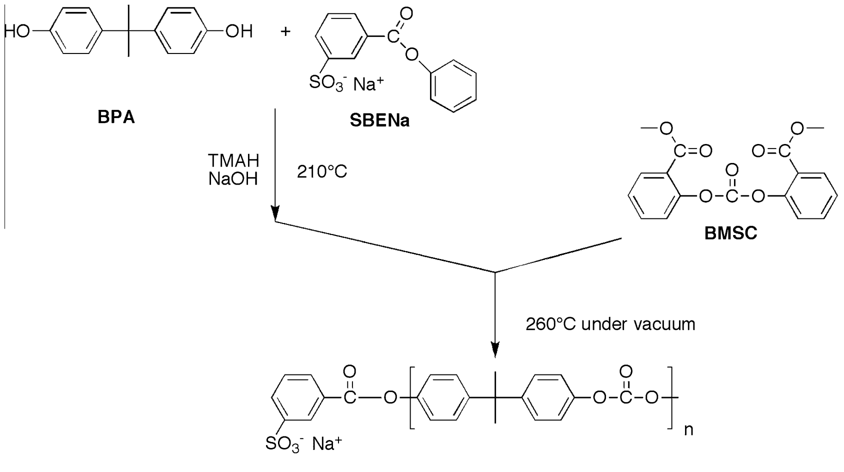

Fig. 1. Polymerization scheme.

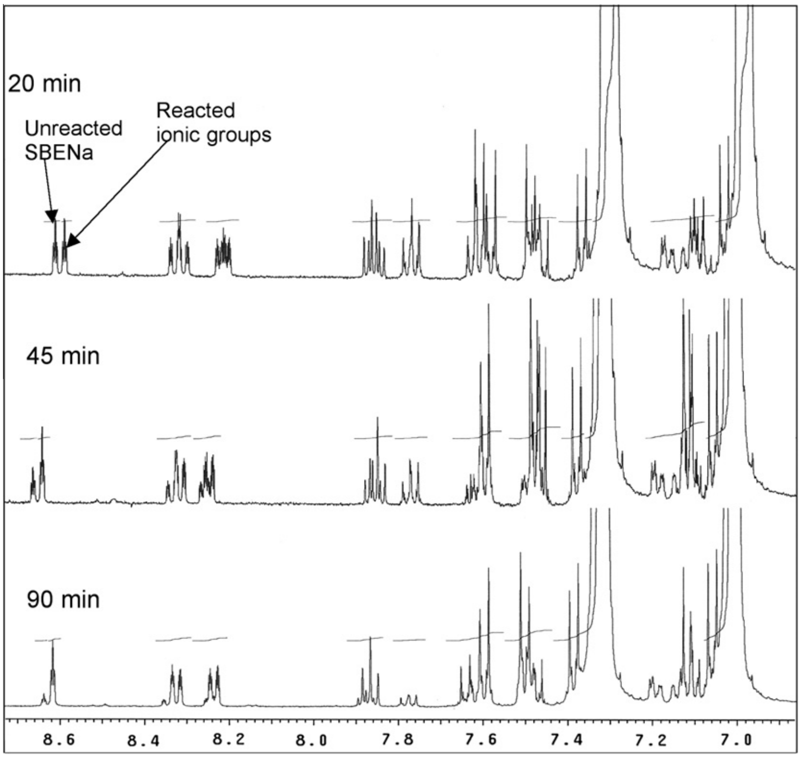

Fig. 2. ^{1}H NMR in d-DMSO of sample at different reaction time during pre-stage using BMSC as monomer.

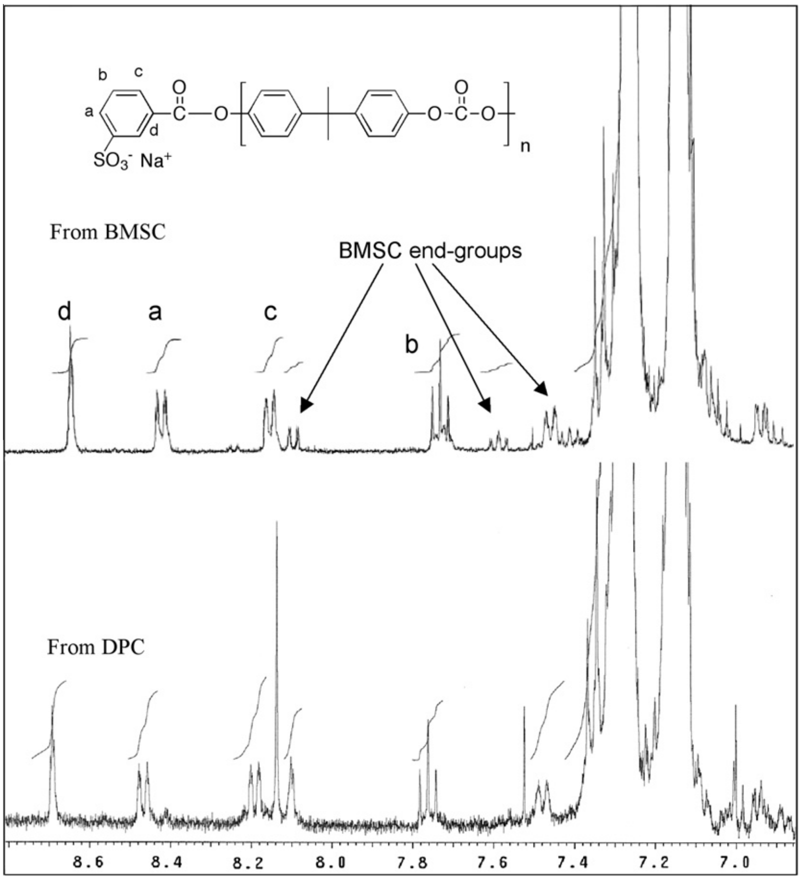

Fig. 3. ^{1}H NMR of the aromatic zone of telechelic ionomers made using BMSC and of the soluble part of that made from DPC in d-DMSO.

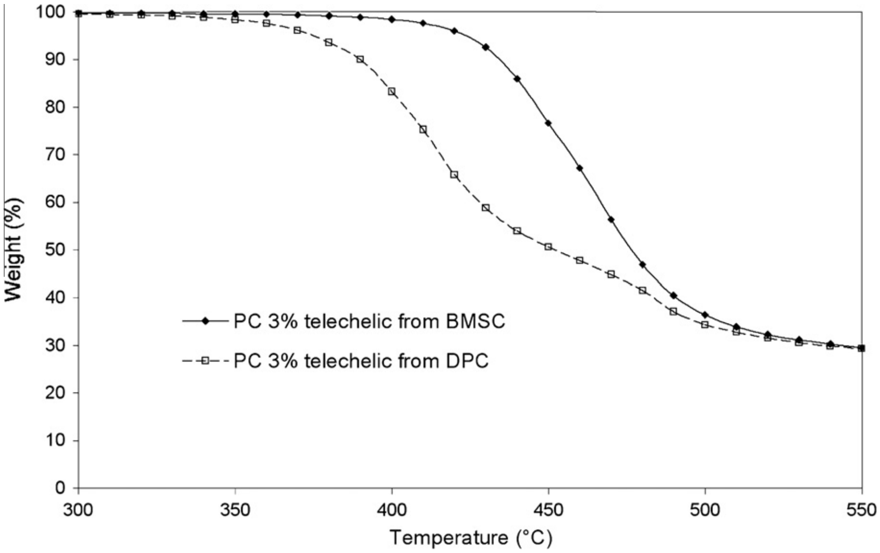

Fig. 4. TGA analysis of telechelic PC made from BSMC and from DPC.

Table 1
Molecular weight, end-groups and thermal properties of sulfonated telechelic ionomers made using BMSC.

SBENa (mol%)[a]	GPC			^{1}H NMR		DSC
	Mw	M_n	Ionic end-groups (mol%)[b]	OH and methyl salycilate end groups (mol%)[b]	M_n	T_g (°C)
0	57,000	25,500	–	1.77	28,700	153
1	65,200	22,200	0.9	1.55	20,730	158
2	69,000	25,300	1.9	1.25	15,630	154
3	70,300	22,700	2.8	1.31	12,360	153

[a] mol% respect to BPA units in the feed.
[b] mol% respect to BPA units in PC samples.

that the addition of salts to the GPC solvent permits to suppress ionic interactions. However, no significant differences were observed in Mw measured by GPC after the salt addition. Gel permeation chromatography is not the appropriate method for the determination of molecular weight in ionic polymers since it is difficult to completely suppress ionic aggregations that are responsible for not reliable molecular weight values. For this reason, all correlations between ionomers properties and molecular weight have been performed just considering the molecular weight calculated by end-group analysis.

DSC analysis shows that ionomers present a higher T_g respect to non-ionic PC. However, there is no direct correlation between ionic content and glass transition temperature since the higher T_g (158 °C) has been observed for the 1 mol% telechelic ionomer. This behavior can be ascribed to the fact that there are two variables affecting T_g, the molecular weight and the ionic content. As

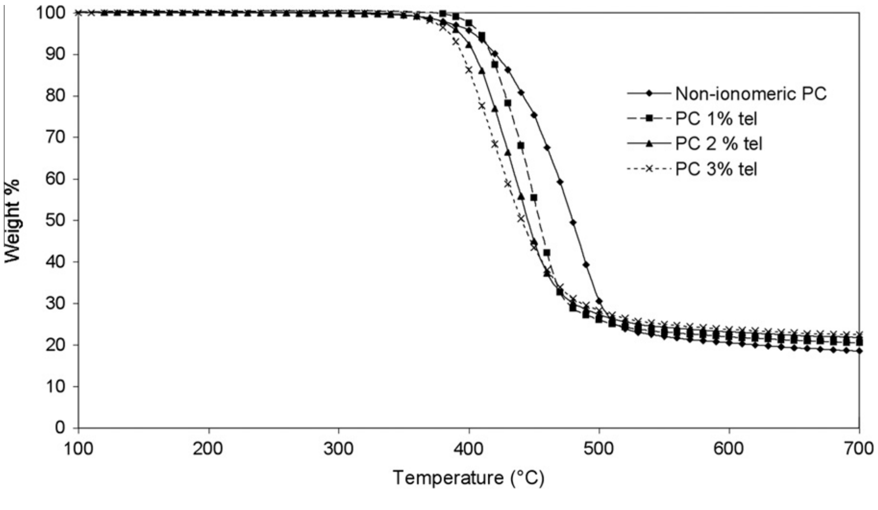

Fig. 5. TGA of telechelic PC made form BMSC.

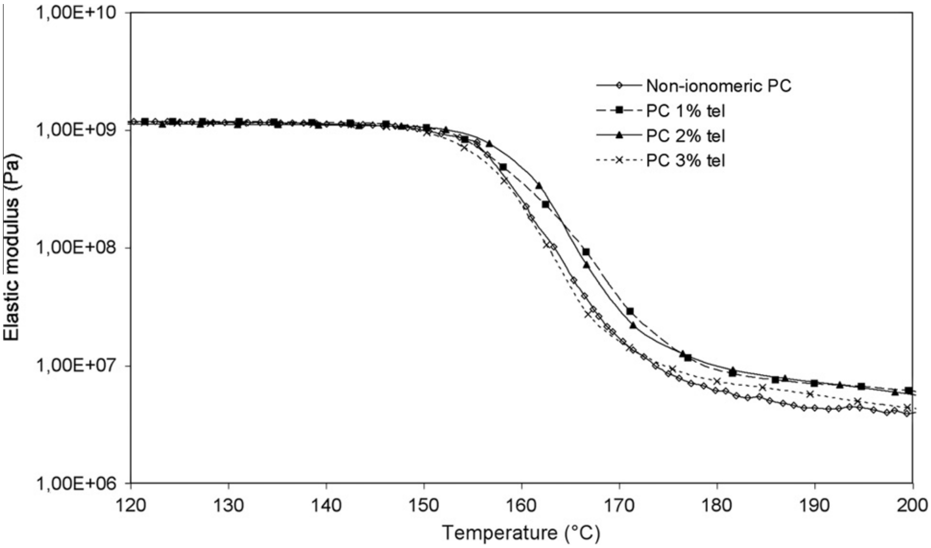

Fig. 6. Storage modulus of telechelic ionomers measured by DMTA.

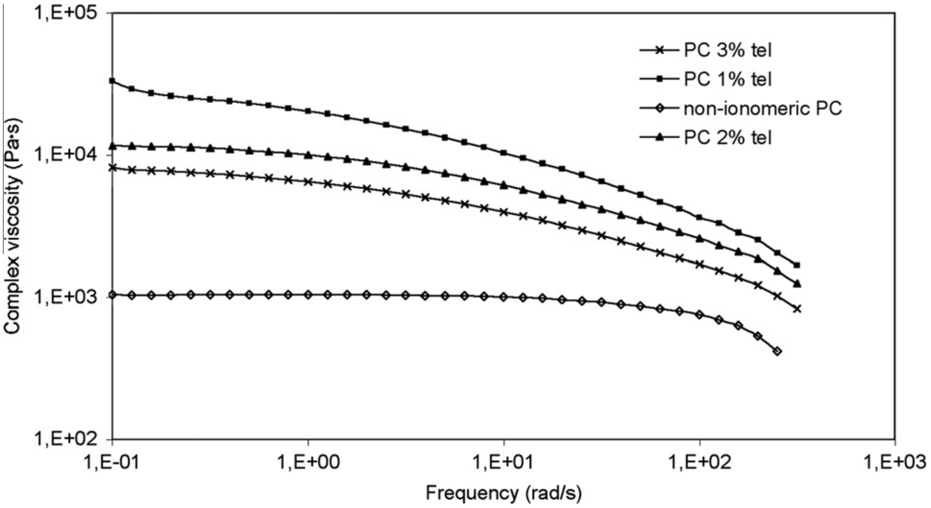

Fig. 7. Complex melt viscosity (η^*) analysis at 260 °C.

discussed previously, for telechelic ionomers the increase in ionic content decreases the molecular weight and therefore the effect of the lower molecular weight for ionomers counterbalance the effect of the ionic content on T_g and a maximum is reached for 1 mol% ionic content.

TGA analysis (Fig. 5) indicates that ionomers are less stable compared to standard PC, nevertheless are stable up to 400 °C well above the typical processing conditions of PC. DSC analysis showed that no crystallinity was present in PC ionomers.

DMTA analysis (Fig. 6) shows that ionomers have higher moduli above T_g respect to PC. However, also in this case no correlation between ionic groups content and storage modulus has been found. Similar to what observed for the glass transition temperature, this behavior can be connected to the presence of two concurrent effects: the modulus increases both with the ionic content and with molecular weight. However, for telechelic ionomers, the increase of the ionic content decreases the molecular weight since the ionic groups act as chain stoppers. Therefore, the most consistent increase in modulus can be observed with ionic content of 1 and 2 mol% while for 3 mol% of ionic end-groups almost no increase in modulus can be observed due to the balance between ionic groups effect and molecular weight decrease.

Melt viscosities of PC ionomers were measured in order to study the effect of ionic aggregation on polymer chain mobility. Dynamic frequency sweep tests at 260 °C (Fig. 7) reveals that all the ionomers have a higher complex viscosity and have a stronger non-Newtonian behavior compared to standard PC. Again, the enhancement in complex viscosity (η^*) cannot be linearly related with the ionic end-group content since the effect of ionic terminals on rheological properties is probably balanced by the lower M_n for ionomers with higher ionic content. For this reason complex viscosity feels the simultaneous effect of ionic groups and molecular weight and all a maximum is reached at lower ionic content (1 mol%).

4. Conclusions

PC sulfonated telechelic ionomers have been successfully prepared by melt polycondensation using bis(methyl salicyl) carbonate, BPA and the phenylester of sulfobenzoic acid sodium salt.

The incorporation of ionic groups is quantitative. This method gives rise to ionomers with high ionic content, with low Fries by-products and with good color respect to telechelic obtained from DPC. The ionomers are stable up to 400 °C and present higher T_g and storage modulus respect to standard PC. This set of balanced properties makes PC ionomers good candidates for PC nanocomposites preparation using organophylic clays. The effect of ionic groups on the clay dispersion in PC/montmorillonite nanocomposites and the characterization of PC-based nanocomposites will be reported in a following paper.

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