

Synthesis and Thermal Properties of Randomly Branched Poly(butylene isophthalate) Containing Sodium Sulfonate Groups

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Received 15 April 2005; accepted 18 June 2005

DOI 10.1002/app.22453

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Randomly branched poly(butylene isophthalate) samples containing sodium sulfonate groups were prepared from dimethyl isophthalate, 3,5-bis(carbomethoxy-carbonyl) benzene sulfonate, tris(hydroxyethyl) isocyanurate, and 1,4-butanediol, according to the well-known two-stage polycondensation procedure. The polymers, containing various amounts of branching units and ionic groups, demonstrated to be soluble in the most common organic solvents, an evidence that gelation was not reached under the polymerization conditions adopted. The thermal behavior was examined by thermogravimetric analysis and differential scanning calorimetry. The sulfonate as well as the

branching units had only a limited effect on the thermal stability, which slightly decreased with respect to pure poly(butylene isophthalate). The analysis carried out using DSC technique showed that the T_m of the copolymers decreased with increasing cation content, differently from T_g , which, on the contrary, increased. Baur's equation was found to describe well the T_m -composition data. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1374–1379, 2006

Key words: polyesters; poly(butylene isophthalate); branched; ionomers; thermal properties

INTRODUCTION

Copolymers have become more and more important in the industrial field, since their physical properties can be tailored to fit specific applications more easily than homopolymers themselves. In fact, physical properties are strongly affected by copolymer composition, structural arrangement of molecular units, sample crystallinity, etc. Consequently, the detailed knowledge of the relationship between polymer structure and properties opens up the possibility of controlled modification and optimization of polymer properties. In particular, the random incorporation of branching units in linear polymers is known to affect drastically several of their properties both in solution and in bulk.¹ Therefore, in previous studies, some of us dealt with the synthesis, molecular, rheological, and thermal characterization of linear and branched poly(butylene isophthalate) (PBI), a polymer belonging to the class of polyalkylene phthalates.^{2–5}

On the other hand, it has been recognized that the introduction of even small amounts of ionic groups into

a chain backbone causes significant changes in the physical properties of polymers. These changes are due essentially to the formation of multiplets or higher-order aggregates (clusters) of ionic materials, which results in physical thermolabile crosslinking.⁶ In this view, previously some of us also synthesized a series of random copolyesters derived from isophthalic acid and containing various amounts of sodium sulfonate groups, which have been characterized from the point of view of molecular, thermal, and rheological properties.^{7,8}

It appeared interesting to complete the previous works by synthesizing polymers characterized by the presence into the PBI backbone both of branching and sodium sulfonate groups (PBI-BS). In this view, two series of PBI-BS samples were prepared, the former containing a fixed amount of branching units and the latter characterized by a constant sulfonated unit content, with the aim of establishing relationship between the thermal properties of PBI-BS and polymer composition.

EXPERIMENTAL

Products

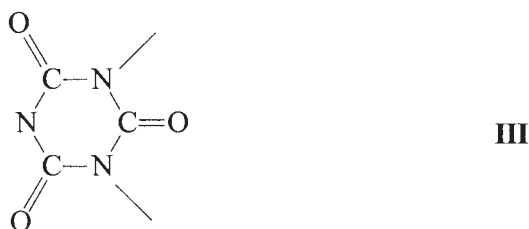
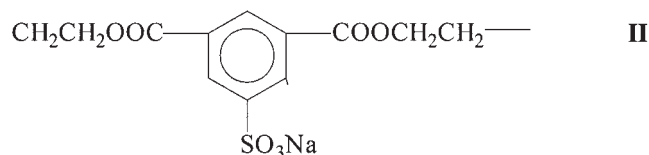
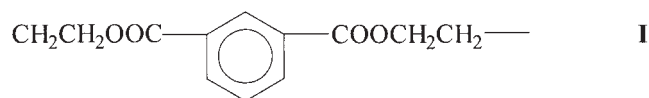
Reagent-grade dimethylisophthalate (DMIP), dimethyl 5-sulfoisophthalate sodium salt (DMSIP), tris(hydroxyl ethyl) isocyanurate (THEIC), and 1,4-bu-

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tanediol were used as supplied by Aldrich; titanium tetrabutoxide ($\text{Ti}(\text{OBu})_4$) (Aldrich) was distilled at reduced pressure before use.

Synthesis of polymers

The copolymers of PBI containing both branching and sulfonated units (PBI-BS) were obtained by the usual two-stage equilibrium polycondensation, starting from different amounts of DMIP, DMSIP (from 2.0 to 9.0 mol % with respect to DMIP), THEIC (from 0.5 to 1.0 mol % with respect to DMIP) and BD, employing $\text{Ti}(\text{OBu})_4$ as catalyst (0.6 g of $\text{Ti}(\text{OBu})_4$ /kg of DMIP). The syntheses were carried out in a 1.8 L stainless-steel batch reactor equipped with a paddle agitator (driven at 30 rpm), with a strain-gauge bridge mounted on the drive shaft to monitor the extent of the polymerization reaction. In the first stage, at atmospheric pressure, the temperature was raised from 160 to 200°C and maintained there until about 90% of the theoretical methanol was distilled off. In the second stage, the pressure was reduced to about 0.5 mbar and the temperature fixed at 220°C. During each run, samples were taken from the bottom of the reactor at different times, to obtain samples with the same composition but different molecular weights. The polymers obtained, because of the use of $\text{Ti}(\text{OBu})_4$ as catalyst and the high reaction temperature, which favor redistribution reactions, are essentially statistical, and the monomeric units are



Viscosimetry

Dilute solution viscosity was measured using Ubbelohde dilution viscometers; measurements were made in CHCl_3 at $30.0^\circ \pm 0.1^\circ$ at four polymer concentration in the range 0.37–1.0 g/dL.

Wide-angle X-ray measurements

Powder X-ray diffraction measurements were carried out at room temperature with a Bragg/Brentano diffractometer system (Philips PW1050/81-PW1710), equipped with a graphite monochromator in the diffracted beam. Cu anode was used as X-ray source.

Thermal analysis

Thermogravimetric analysis was carried out both in air and under nitrogen atmosphere using a Perkin-Elmer TGA7 apparatus (gas flow, 50 mL/min) at $10^\circ\text{C}/\text{min}$, heating rate up to 900°C .

Calorimetric measurements were performed by means of a Perkin-Elmer DSC7 instrument equipped with a liquid subambient accessory and calibrated with high purity standards (indium and cyclohexane). The external block temperature control was set at -60°C . Weighed samples (c.a. 10 mg) were encapsulated in aluminum pans and heated to about 40°C above fusion temperature, at a rate of $20^\circ\text{C}/\text{min}$ (first scan) and then rapidly quenched to -30°C . Finally, they were reheated from -30°C to a temperature well above the fusion temperature of the sample, at a heating rate of $20^\circ\text{C}/\text{min}$ (second scan). The glass-transition temperature T_g was taken as the midpoint of the heat capacity increment Δc_p associated with the glass-to-rubber transition. The melting temperature (T_m) was determined as the peak value of the endothermal phenomenon in the DSC curve. The specific heat increment $\Delta c_{p,r}$ associated with the glass transition of the amorphous phase, was calculated from the vertical distance between the two extrapolated baselines at the glass transition temperature. The heat of fusion of the crystal phase was calculated from the area of the DSC endotherm. Repeated measurements on each sample showed excellent reproducibility.

RESULTS AND DISCUSSION

At room temperature PBI-BS copolyesters appear as semicrystalline solids. The solubility of the samples was checked in various solvents. All the samples were found to be well soluble at room temperature in the most common organic solvents, i.e., chloroform, tetrachloroethane, methylene chloride, etc. This is an evidence that the gel point was never reached, proving that a good polymerization control was obtained. As concerns the dilute solution behavior, it is well-known that the intrinsic viscosity $[\eta]$ of a polymer is correlated to the molecular weight by means of the Mark-Houwink equation. The intrinsic viscosity value can be obtained using both Huggins and Kramer plots, i.e., by extrapolating η_{sp}/c and $(\ln \eta_r)/c$ to zero concentration. Nevertheless, for the polymers containing ionic groups, the two curves usually do not have a

TABLE I
Composition and Dilute Solution Data of PBI-BS
Random Copolymers

| Polymer | Trifunctional units (mol %) | Ionic group content (mol %) | η_{sp}/c^a |
|----------|-----------------------------|-----------------------------|-----------------|
| PBI | 0 | 0 | 1.068 |
| PBI-B1S2 | 0.50 | 5.00 | 0.652 |
| PBI-B1S3 | 0.50 | 9.00 | 0.433 |
| PBI-B2S1 | 0.75 | 2.00 | 1.040 |
| PBI-B2S2 | 0.75 | 5.00 | 0.632 |
| PBI-B2S3 | 0.75 | 9.00 | 0.408 |
| PBI-B3S1 | 1.00 | 2.00 | 1.180 |
| PBI-B3S2 | 1.00 | 5.00 | 0.710 |
| PBI-B3S3 | 1.00 | 9.00 | 0.338 |

^a At $c = 0.5$ g/dL.

linear trend and do not cross each other at zero concentration, because of molecular aggregations in solution.⁸⁻¹⁰ This trend was indeed observed for all the PBI-BS copolymers and therefore, for each sample, the value of η_{sp}/c at $c = 0.5$ g/dL has been reported in Table I and taken as an index of the molecular weight.

It was found that for each copolymer, the η_{sp}/c value at $c = 0.5$ g/dL increased as the polymerization time was increased, indicating that samples characterized by increasing molecular weight are obtained at increasing polymerization time. The polymers synthesized are listed in Table I together with the η_{sp}/c data at $c = 0.5$ g/dL.

The copolyesters were afterwards examined by thermogravimetric analysis and differential scanning calorimetry. As is well known, the molecular weight of a polymer can influence its thermal properties, and therefore, a preliminary investigation was performed to evaluate this effect: thermal measurements carried out on sample with the same composition but different η_{sp}/c value, gave practically identical results. For exactness, the data reported here refer to the sample with the highest molecular weight (i.e., the highest

TABLE II
Thermogravimetric and Calorimetric Data of PBI-BS
Random Copolymers

| Polymer | T_{id} (°C) | T_{max} (°C) | 1 st scan ^a | | 2 nd scan | |
|----------|---------------|----------------|-----------------------------------|--------------------|----------------------|-----------------------|
| | | | T_m (°C) | ΔH_m (J/g) | T_g (°C) | Δc_p (J/g °C) |
| PBI | 382 | 401 | 142.9 | 52 | 25.2 | 0.366 |
| PBI-B1S2 | 373 | 388 | 134.2 | 46 | 30.7 | 0.360 |
| PBI-B1S3 | 364 | 378 | 127.2 | 41 | 32.6 | 0.369 |
| PBI-B2S1 | 374 | 390 | 140.4 | 49 | 28.2 | 0.374 |
| PBI-B2S2 | 368 | 383 | 134.7 | 46 | 30.9 | 0.363 |
| PBI-B2S3 | 361 | 372 | 126.5 | 42 | 32.4 | 0.362 |
| PBI-B3S1 | 372 | 387 | 139.9 | 50 | 27.9 | 0.358 |
| PBI-B3S2 | 366 | 378 | 134.0 | 48 | 31.4 | 0.365 |
| PBI-B3S3 | 357 | 366 | 127.0 | 40 | 33.0 | 0.371 |

^a On samples annealed for 4 days at 100°C.

values of η_{sp}/c) available for each composition. The investigation on the thermal stability was carried out both in air and under nitrogen atmosphere. Typical curves of some copolymers recorded in air are shown in Figure 1, together with that of linear unsulfonated PBI: in particular, Figure 1(a) reports the thermogravimetric traces of a series of copolymers containing a fixed amount of branching units (0.75 mol %) and increasing sulfonated unit content, whereas Figure 1(b) displays the TGA curves of copolymers with 5 mol % of ionic groups and different amount of branching units.

From the thermogravimetric curves in air, the temperature of initial decomposition (T_{id}) and the temperature corresponding to the maximum weight loss rate (T_{max}), collected in Table II, were also determined.

It can be seen that in all cases the weight loss takes place practically in one-step and a solid residue is only present for the samples containing the highest amount of counits. Moreover, Figure 1 shows that there are effects due to the presence of sodium sulfonate groups or branching point: a little shifting towards lower

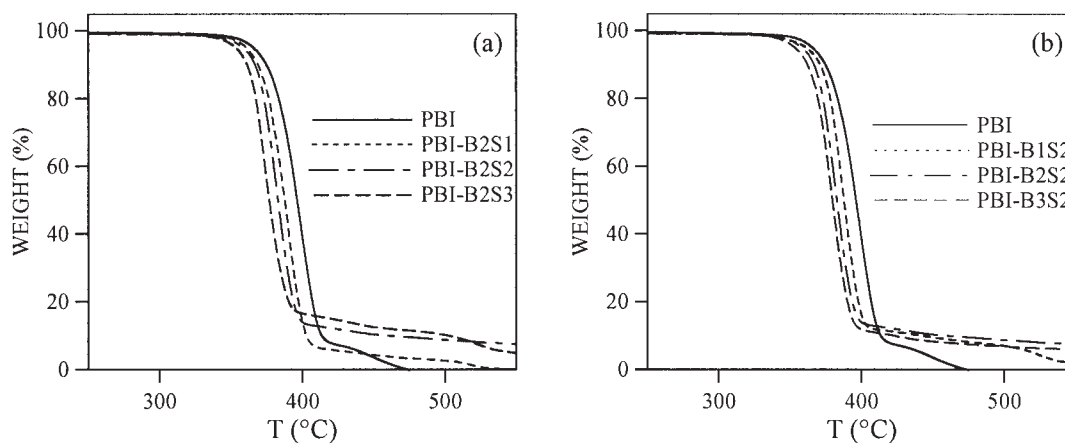


Figure 1 TGA curves of PBI and PBI-BS random copolymers heated at 10°C/min in air.

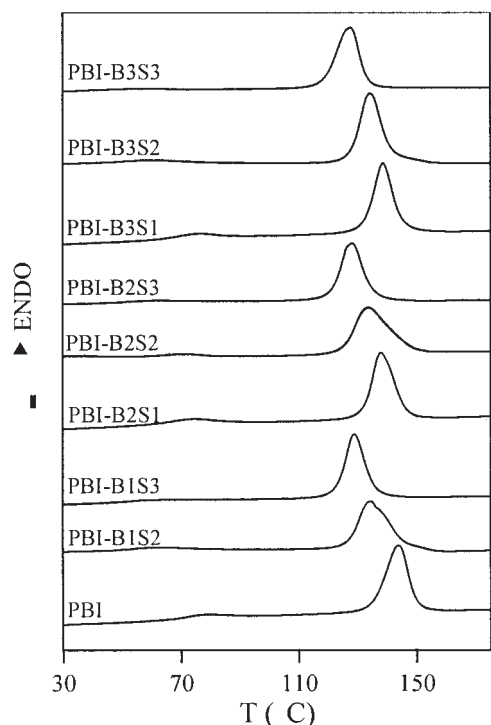


Figure 2 Calorimetric curves of PBI and PBI-BS copolymers annealed for 4 days at 100°C.

temperatures of the maximum rate of weight loss is observed, independently of the nature of the counits present into the polymeric chain of PBI. Anyway, it has to be noted that the thermal stability stays good, all the samples being stable up to 320°C. An analogous trend was found by some of us in investigating PBI containing SO_3Na groups only.⁷ On the contrary, the analysis of the effect of branching point on the thermal stability of PBI carried out previously evidenced no significant variations.⁵ Nevertheless, it has to be pointed out that those samples were characterized by

a lower content of branching units and the absence of ionic groups.

Similar results on the thermal stability of PBI-BS copolymers were obtained by means of TGA measurements carried out under nitrogen atmosphere.

As far as the calorimetric results are concerned, it is well-established that the melting behavior of a polymer is affected by its previous thermal history; therefore, to provide the same heat treatment to all the samples investigated, prior to thermal analysis the specimens have been annealed at 100°C for 4 days. The DSC traces of such samples are reported in Figure 2 and the data obtained in Table II.

In all cases, a glass transition and a melting endotherm are evident. In the copolymers, peak location appears to depend on composition; furthermore, the increase in the amount of comonomer added to PBI chain leads to a slight reduction of the heat of fusion, indicating a reduced level of crystallinity in the copolymers with respect to the homopolymer. Lastly, in the copolymers, the endotherm region is broader, suggesting the presence of a larger distribution of crystallites with different degree of perfection. In Figure 3(a), the T_m values are plotted as a function of butylene isophthalate (BI) unit content: the melting point depression with the increment of counit content is typical of random copolymers in which only one counit takes part in the crystallization process.

In fact, as can be seen, T_m decreases with the increment of sulfonated or branching counit content and the data are found to lie on the same curve. As T_m depends exclusively on the molar fraction of butylene isophthalate content and not on the specific chemical characteristics of the counits, the exclusion of sulfonated or branching counits from the crystalline lattice is highly probable. To check the unit cell structure of the crystalline phase in the samples under investigation, X-ray diffractometry measurements were per-

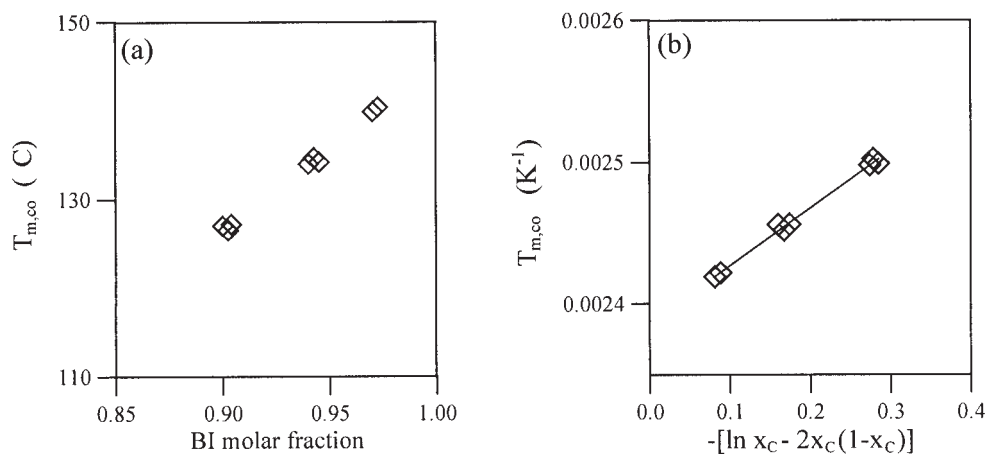


Figure 3 (a) Melting temperatures as a function of composition; (b) $1/T_m$ -composition plots according to Baur's equation.

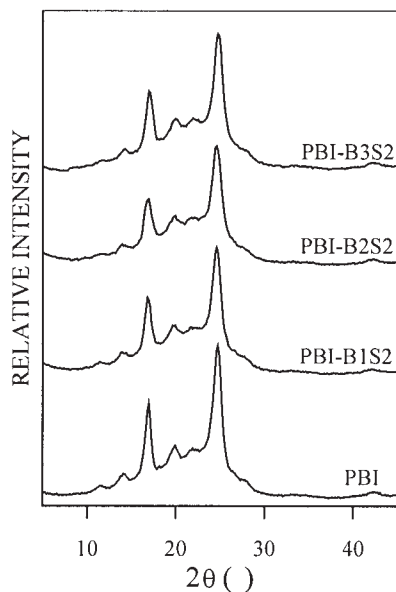


Figure 4 Wide-angle X-ray spectra of PBI and PBI-BS random copolymers.

formed. As an example, the diffraction curves for PBI and PBI-BS copolymers containing a fixed amount of sulfonated units (5 mol %) and increasing branching unit content are reported in Figure 4.

The XRD pattern of linear unsulfonated PBI homopolymer exhibits a well-defined set of crystalline diffraction peaks. The PBI-BS copolymers are characterized by X-ray spectra, which match well with that of PBI, proving that the crystal structure that develops in the copolymers corresponds to the characteristic lattice of PBI. Similar results were obtained for all the other PBI-BS copolymers.

The melting point reduction can be examined to estimate the equilibrium melting temperature T_m^0 and the equilibrium heat of fusion ΔH_m^0 of the crystallizable unit. Flory's treatment,¹¹ derived assuming that the fusion concerns the disappearance of long sequences of crystallizable units, underestimates the melting point depression of random copolymers. As a matter of fact, the concentration of long sequences decreases with increasing coint content, and the experimental T_m values are consequently lower than those postulated by the theory.

On the contrary, the following equation, proposed by Baur,¹² takes into account the effect of sequence length:

$$1/T_{m,co}^0 = 1/T_m^0 - (R/\Delta H_m^0)(\ln x_C - 2x_C(1 - x_C)) \quad (1)$$

where $T_{m,co}^0$ is the melting temperature of a random copolymer with mole fraction x_C of crystallizable comonomer C, T_m^0 is the equilibrium melting temperature of the homopolymer (in this case PBI) and R is

the universal gas constant. On the basis of eq. (1) the $T_{m,co}^0$ s were reciprocally plotted against $-\ln x_C - 2x_C(1 - x_C)$ in Figure 3(b) and the equilibrium melting temperature and the heat of fusion for the completely crystalline PBI were extrapolated. As can be noted, the plot shows a good linearity and this result can be considered an indirect proof of the random nature of the copolymers investigated. The estimated T_m^0 and ΔH_m^0 were found to be 146°C and 93 J/g, respectively, in agreement with the values reported in the literature.^{13,14}

As is well known, a partially crystalline material usually exhibits a different glass transition behavior than the completely amorphous analogous. In fact, although some conflicting results are reported in the literature,¹⁵ crystallinity usually acts like crosslinking and raises T_g through its restrictive effect on the segmental motion of amorphous polymer chains. Therefore, to study the influence of chemical structure on the glass transition of random copolymers, the phenomenon should be examined in the total absence of crystallinity. In this view, all the samples under investigation were subjected to rapid cooling (quenching) from the melt (see the Experimental section for the details). In all cases, the DSC curves after melt quenching are characterized only by an intense endothermal baseline deviation associated with the glass transition phenomenon. The values of glass transition temperature are collected in Table II and plotted in Figure 5 as a function of ionic group content.

As can be seen, the glass transition temperature is influenced by the amount of SO_3Na -containing units in the chain: one can observe that the T_g values increase as sulfonate unit content is increased. As re-

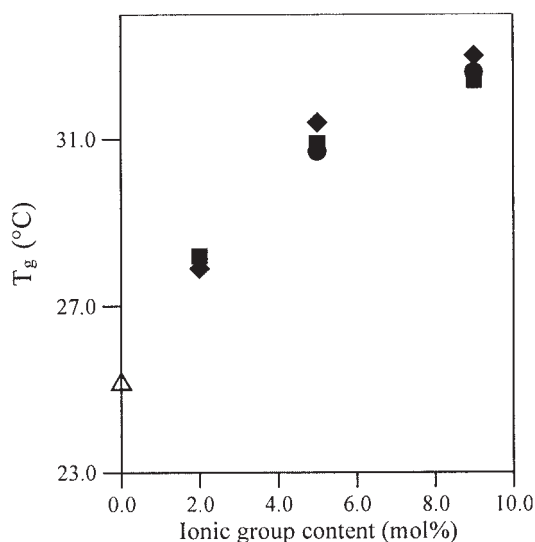


Figure 5 T_g as a function of ionic group content for PBI-BS copolymers with different amount of trifunctional units (●, ■, ◆, refer to 0.50, 0.75, 1.00 mol %, respectively).

ported in the literature, two main reasons are invoked to explain the increase of T_g of ionomers: the ionic interactions leading to ion-clustering or physical crosslinks and the introduction of bulky sulfonate groups and from hydrogen bond interaction. As demonstrated previously,^{7,16,17} in the case of polymeric samples containing SO_3Na groups, the contribution from ionic aggregations seems to be negligible, the increment of T_g appearing more likely to be the result of internal chain stiffening due to the presence of sulfonate comonomeric units. Therefore, it is highly probable that ion-clustering effects can be ruled out also for the samples under investigation. As far as the effect of long branching on the glass transition temperature is concerned, the comparison of T_g 's of copolymers characterized by a fixed amount of sulfonate units and variable content of branching ones (see Fig. 5) evidences that it is substantially unaffected by the variation of the amount of trifunctional units, as previously found on analyzing branched PBI copolymers.⁵

CONCLUSIONS

The results obtained showed the possibility of easily synthesizing in bulk poly(butylene isophthalate) copolyesters containing both sulfonate groups and long ramifications, avoiding crosslinking, as demonstrated by the good solubility in many common solvents. As concerns the thermal properties, composition appears to be the prominent parameter in determining the characteristics of the samples under investigation. The introduction in the polymeric chain of ionic groups and long ramifications influenced only slightly the thermal stability. The statistical nature of the samples was supported by T_m -composition plots, which are

typical of statistical copolymers, and by the applicability of Baur's equation. No effect was found on the polymer phase behavior after melt-quenching, the PBI-BS copolymers appearing as amorphous samples, similarly to pure PBI. On the other hand, the glass transition temperature showed an increment, mainly due to the introduction of bulky sulfonate units in the backbone, whereas the effect of the presence of ramifications seemed to be negligible.

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