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Modification of PET by Reactive Blending with Sulfonated Esters, 1

Synthesis and Characterization of PET-Ionomers

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Summary: A new route of synthesis of ionomers has been found: when PET is treated in a Brabender with a sulfonated ester, transesterification reactions occur providing a new polymer, characterized by a lower molecular weight and ionic groups as chain ends. The presence of the ionic groups causes strong modifications in the thermal properties of the material.

Introduction

Ionomers are macromolecules containing a small number (typically up to 10-15 mol%) of ionic groups chemically bound to a non-polar chain. The incorporation of ions can widely modify the physical mechanical properties of the material1): for this reason, there is an increasing interest both from an academic and an industrial point of view on this subject.

The traditional ionomers are characterized by ionic groups irregularly distributed, at best at random, along the polymer chains. The formation of ionic aggregations and their relatively high stability are responsible for the unusually high melt viscosity and long relaxation times: therefore improved mechanical properties can be easily obtained2). However, the ionic associations are impeded by the entanglements of the main polymeric backbone and by the irregular placement of the self-associating groups. This may result in a poorly defined chain network.

A better insight into the mechanism of ion aggregation and its effect on bulk properties should be obtained from macromolecules containing a constant number of regularly placed ionic groups. This is the case of the halato-telechelic ionomers, a peculiar family

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of ionomers characterized by ionic groups located only at the chain ends. Research on solid-state mechanical behavior$^{3)}$, melt rheology$^{4)}$ and morphology$^{5)}$ of these polymers has been recently carried out: also in this case the properties appeared very interesting and strictly connected to the presence of ionic aggregations. In this case, the chains, end-capped with a peculiar ionic group, are largely independent of each other, making the self-association process much easier.

In general, the preparation of halato-telechelic polymers is based on the ionization of the end-groups of telechelic polymers$^{6)}$. In this work a new approach of synthesis, based on the reactive blending between a high molecular weight polymer and a monofunctional ionic compound, has been studied; this route, that causes chain scissions, has been applied to poly(ethylene terephthalate) (PET). Some properties of the polymers obtained are investigated.

Experimental

Materials

Poly(ethylene terephthalate) (PET-0) ([η]=0.80 dL/g in 1,1,2,2-tetrachloroethane/phenol, 60/40 wt/wt at 30.0°C) was a commercial product supplied by EniChem S.p.A., Italy. 4-Hydroxybutyl benzoate (HBB) was synthesized as reported in literature$^{7)}$. 2-Sulfobenzoic acid cyclic anhydride (from Aldrich), tetrabutylorthotitanate (TBT) (from Merck) and benzyltriethylammonium chloride (from Aldrich), were used as received. The solvents used were reagent grade and no further purification was made.

Measurements

IR spectra were recorded on a Bruker IFS 48 FT-IR instrument. ^{1}HNMR spectra were recorded on a Varian XL-300 spectrometer (chemical shifts are given in ppm downfield from tetramethylsilane). The samples were dissolved in a mixture of $CDCl_3/CF_3COOD$ 80/20 v/v.

The viscosities were measured at 30.0°C with an Ubbelhode viscometer using a 0.05 M solution of benzyltriethylammonium chloride in 1,1,2,2-tetrachloroethane/phenol 60/40 wt/wt. Intrinsic viscosity was calculated on the basis of viscosity measurements of dilute solutions (at least four different concentrations for each sample).

Thermogravimetric measurements were carried out in nitrogen atmosphere using a

Perkin Elmer TGA7 (gas flow 20 mL/min) at 20°C/min from 50°C to 900°C. The calorimetric analysis was performed in a Perkin Elmer DSC7 apparatus, calibrated with high purity standards. Isothermal crystallizations were performed after melting at 250°C for 1 min and fast cooling from 250°C to the selected crystallization temperature (T_C). T_C range varies from 190°C to 225°C depending on the sample. After the crystallization the samples were heated at 10°C/min to 250°C.

Synthesis of the Sodium Salt of n-Butyl 2-Sulfobenzoate (2-SBABE)

10.0 g (54.3 mmol) of 2-sulfobenzoic acid cyclic anhydride and 70 mL of 1-butanol were kept under reflux for 15 min. After cooling to room temperature the solution was neutralized with NaOH 1 N in methanol. Upon evaporation of the solvent to dryness 12.6 g of crude 2-SBABE were obtained; crystallization from 1-buthanol gave 11.4 g (75%) of white crystalline 2-SBABE (m.p. 200 at 10°C/min in DSC). The synthesis is described in the scheme 1.

IR (NaCl): 1730 cm^{-1} (Ar-CO-O-)
1250 cm^{-1} ($-SO_3Na$)
^{1}H-NMR spectrum ($CDCl_3/CF_3COOD$ 80/20 v/v) is reported in Figure 2.

Reactive Blending

A Brabender mixer (Plasti-Corder PL2000) equipped with two counter-rotating, double winged rotors was used for the melt mixing. The rotor speed was kept at 60 rpm throughout the overall reaction time. During the blending, the mixer bowl was fluxed with a moderate stream of dry nitrogen to avoid the hydrolytic degradation of the polymer.

50 g of PET-0, previously dried at 120°C under vacuum overnight, and 20 μL of TBT as catalyst, were mixed at 275°C for 2 min. After this time 2-SBABE or HBB was added to the melt polymer in variable quantity as described in Table 1. The mixing time was 20 min for all the experiments.

The polymers were purified by dissolution in 1,1,1,3,3,3-hexafluoro-2-propanol/dichloromethane (HFIP/DCM) (30/70 wt/wt) solution and precipitated in methanol. Before the reaction, polymers were dried at 120°C under vacuum over night.

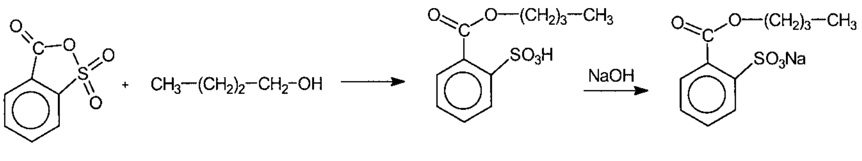
Results and Discussion

Synthesis of 2-SBABE

Attempts to synthesize a series of sulfobenzoic esters have been carried out, by starting from the corresponding sulfobenzoic acids and different aliphatic alcohols. However the first attempts were unsuccessful, due to the difficulty of obtaining pure products. For example, the synthesis of the 3-sulfobenzoic acid methylester sodium salt was performed starting from the 3-sulfobenzoic acid and methanol in the presence of an acid catalyst, followed by a neutralization step with CH_3ONa: the result was a mixture of products, including the starting material in large amount.

These results can be attributed to the presence of sulfonic or sulfonated groups in the benzoic ring, that drastically modify the reactivity of –COOH and $-COOCH_3$8). In particular, van Duin observed that in a substituted benzoic acid, the rate of the esterification of –COOH is low and the rate of saponification is high when a sulfonic substituent is present, in particular in *para* or *meta* positions. On the contrary, $-SO_3H$ in *ortho* causes an increment in the acidity of –COOH, inducing a relatively more rapid esterification, and $-SO_3Na$ in *ortho* decreases the saponification rate of –COOR. For these reasons, our attention was focused only on the synthesis of *ortho* substituted esters.

As suggested in literature8), these new reactions were performed by starting from the 2-sulfobenzoic acid cyclic anhydride. Indeed, the synthesis of 2-SBABE, described in the Scheme 1, gives readily a pure product, with a yield of about 75%. Other esters were synthesized following the scheme 1 and varying only the length of the aliphatic chain of the alcohol: however, in this context only the results obtained by using the 2-SBABE for the reactive blending are reported.



Scheme 1: Synthesis of 2-SBABE.

Preparation of PET-Ionomers

As described in the experimental part, ionomers were prepared by reactive blending in a Brabender mixer. The polymers obtained and the intrinsic viscosity data are reported in Table1.

Figure 1 reports the trend of the torque, measured during the blending, as a function of mixing time, for PET-0 and PET-I1. In the first two minutes the decrement of the torque is similar for the two polymers and can be attributed to the polymer melting and to the reactions induced by the presence of TBT. After that, the torque reaches a plateau for PET-0. The addition of 2-SBABE in PET-I1, instead, causes a further decrement of the torque. This behavior has been observed also for the other samples obtained in Brabender.

Table 1: Description of the polymers obtained by reactive blending.

Sample	**Reagent added to PET-0 (mol%[a])**	**mol% [a] of sulfonated units bonded to PET**	**[η] (dL/g)**
PET-0	-	-	0.80
PET-0*[b]	-	-	0.60
PET-I1	2-SBABE (2.8)	0.60[c]	0.36
PET-I2	2- SBABE (5.0)	2.5 [c]	0.26
PET-I3	2- SBABE (10.0)	5.0 [c]	0.19
PET-1	HBB (1.0)	-	0.46
PET-2	HBB (1.5)	-	0.27

[a] Calculated respect to PET repeating units.
[b] Sample of PET-0 treated in Brabender
[c] Calculated from ^{1}H-NMR spectra.

The intrinsic viscosity data, reported in Table 1, give relevant information to understand the behavior observed. For PET-0 the intrinsic viscosity decreases from 0.80 to 0.60 dL/g after the treatment in Brabender, suggesting the occurrence of a reaction with the catalyst with exchange of the -OBu groups. For the ionomers the decrement of the intrinsic viscosity is larger and is a function of the amount of sulfonated ester added. A similar decrement of molecular weight occurs also in the case of the addition of HBB to PET-0 in Brabender. These results suggest that ester exchange reactions take place that lead to chain scission during the mixing at high temperature.

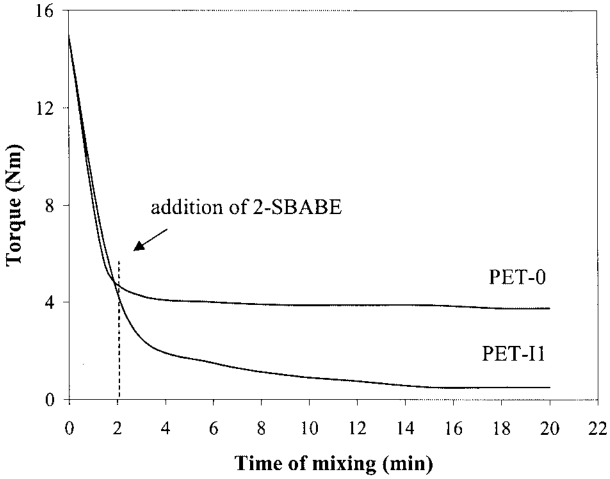


Fig. 1: Trend of the torque as a function of the mixing time for two samples treated in Brabender.

Figure 2 reports the ^{1}H-NMR spectra of *i)* 2-SBABE, *ii)* crude PET-I1 and *iii)* purified PET-I1. By analyzing the aliphatic region, it is possible to observe that 2-SBABE shows three signals (*b, c* and *d*) in the aliphatic range from 0.9 to 2.0 ppm and a triplet (*a*) at 4.3 ppm. In the same region, crude PET-I1 exhibits new signals respect to PET-0: *a, b, c* and *d*, with small intensity, correspond to the original signals of 2-SBABE and *a', b', c'* and *d'* are signals shifted to lower fields. The purified PET-I1 presents only the shifted signals *a', b', c'* and *d'*. As the purification process eliminates the 2-SBABE unreacted, it is reasonable to attribute in the polymer spectrum the *a, b, c* and *d* signals to the unreacted 2-SBABE and the shifted multiplets *a', b', c'* and *d'* to the butyl units bonded to the polymer.

By integration of these signals, it results that in the crude PET-I1 the overall percentage of the aliphatic groups is equal to 2.3 mol% and their percentage bonded to PET 1.8

mol%. Therefore, the 76% of 2-SBABE reacts in Brabender. The decrement of the measured quantity of 2-SBABE respect to the initial quantity used (2.3 vs. 2.8 mol%) could be due to the a partial degradation of 2-SBABE when it is treated for 20 min at 275°C. Finally, in the purified PET-I1, the percentage of the aliphatic groups bonded to PET decreases to 1.5 mol%. Then, the purification process eliminates a certain amount of oligomers.

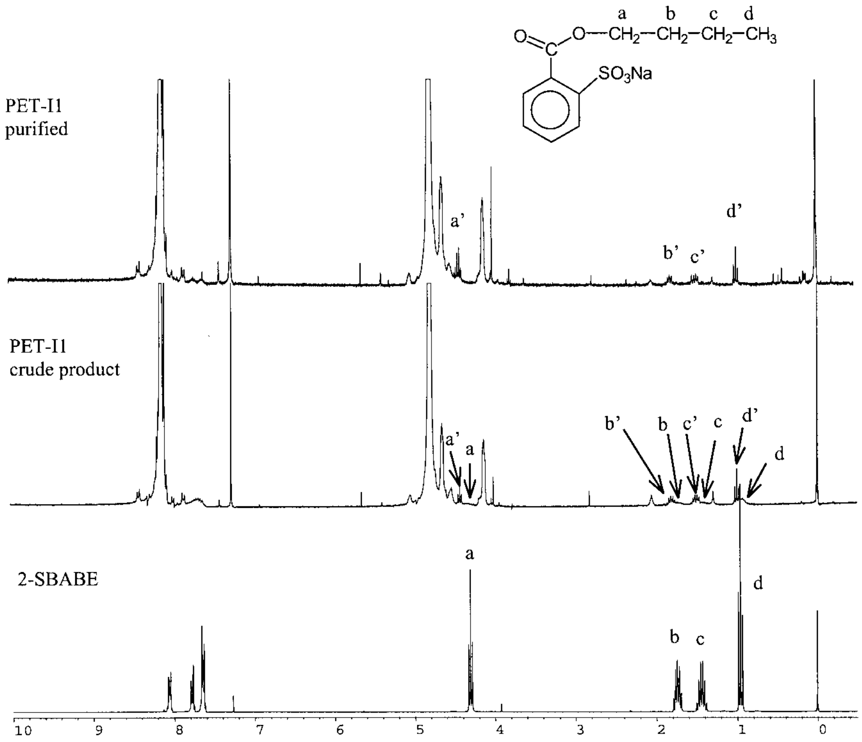
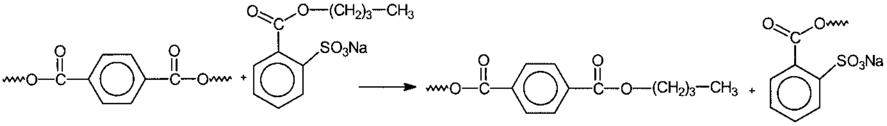


Fig. 2: ^{1}H-NMR spectra of *i)* 2-SBABE, *ii)* crude PET-I1 and *iii)* purified PET-I1.

By analyzing the aromatic region, crude and purified PET-I1 present new signals respect to PET-0, in the range from 7.6 to 8.2 ppm. The integration of these signals in the purified polymer indicates the effective amount of sulfonated units present in the ionomer and the final results are reported in Table 1 for all the analyzed samples. These data have been also confirmed by elemental analysis.

These quantities result lower that those calculated by integration of the corresponding butyl signals, probably due a selective extraction of sulfonated oligomers during the purification process. As a confirmation, the ^{1}H-NMR spectrum of the fraction of polymer soluble in methanol was recorded: the results indicate the presence of unreacted 2-SBABE and PET with bonded sulfonated groups. Therefore, the presence of ionic groups increases the solubility of sulfonated oligomers and a fraction of them is lost during the purification step.

As a first conclusion, the ^{1}H-NMR analysis clearly indicates the presence of new sulfonated and aliphatic moieties in PET-I1, I2 and I3: therefore, 2-SBABE is good reagent to insert ionic groups by reaction with the ester linkages of PET. This reaction takes place by a chain scission mechanism, as shown in the scheme 2, and causes a decrement of molecular weight, confirmed by the torque trend (Figure 1) and the intrinsic viscosity data (Table 1).



Scheme 2: Chain scission mechanism for the insertion of 2-SBABE.

As shown in Table 1, the amount of sulfonated units present in the final ionomers are much lower respect to the initial amount of 2-SBABE used This means that the transesterification reaction is not complete, especially in the case of PET-I1. This is evident also by comparing the characteristics of the ionomers with those of the samples obtained by using HBB in the Brabender. Samples PET-2 and PET-I2, for example, are characterized by very similar intrinsic viscosity, but PET-2 is obtained by adding only 1.5 mol% of HBB respect to the 5.0 mol% of 2-SBABE used for PET-I2. This result confirms that the presence of sulfonated groups modify the reactivity of the ester in the transesterification reactions[8)].

Thermal Analysis

The thermal analysis, carried out by TGA and DSC, has been performed in order to observe if the presence of a small quantity of sulfonated units as chain ends in the PET backbone can influence the thermal behavior, as described in literature for the randomly sulfonated polymers9).

Some results of the thermogravimetric analysis are reported in Table 2: it is possible to observe that onset temperatures, related to the degradation process of the polymer backbone, slightly increase passing from the pure PET (PET-1 and 2 samples) to PET-I1 and PET-I2, despite of the decrement of molecular weight. This increment, instead, is associated to the increasing of the sulfonated units content and can be attributed to the formation of physical crosslinks originated by the ionic units10). Only for PET-I3, characterized by the highest ionic content, it is not evident an increment of the thermal stability, probably due to its very low molecular weight.

Table 2: Results of the thermal analysis (TGA and DSC), together with the intrinsic viscosity data.

Sample	TGA Onset (°C)	Tm° (°C)	[η] (dL/g)
PET-I1	437	269.2	0.36
PET-I2	443	272.2	0.26
PET-I3	429	274.7	0.19
PET-1	430	275.7	0.46
PET-2	430	271.7	0.27

The DSC analyses have been performed in isothermal conditions and the thermal behavior of PET ionomers has been compared to that of PET homopolymers. It is important to underline that this comparison have to be carried out on samples characterized not only by similar molecular weight, but also by similar thermal treatment in Brabender. In fact, the polymers, treated in Brabender and subjected to shear in the melting state, are characterized by higher crystallization rate respect to that of the same polymers, with identical molecular weight and not treated in Brabender11). This is the effect of local alignments of macromolecular chains, that act as initiator of crystallization process. This is the reason why PET-1 and 2 have been prepared in

Brabender by mixing PET-0 and HBB.

The melting process is characterized by a double peak, that is due to recrystallization phenomena occurring during the fusion12). The temperature of the first melting peak has been reported in the Hoffman-Weeks plot13) as a function of the crystallization temperature, in order to calculate, by extrapolation, the equilibrium melting temperature (Tm°). The Tm° values are reported in Table 2, together with the intrinsic viscosity data: it is noteworthy that for the ionomers PET-I1, I2 and I3 Tm° increases as the intrinsic viscosity decreases. This behavior is unexpected and in our opinion is due to the presence of strong ionic associations between polymer chains in the solid state14). This observation confirms the results obtained by TGA analysis.

The isothermal crystallization curves have been analyzed in order to determine the crystallized fraction (X) as a function of the crystallization time (t): these data have been analyzed by the Avrami equation15):

$$X = 1 - \exp(-K\, t^{n})$$

where K is a kinetic constant used to compare the crystallized rates of the analyzed polymers at the same undercooling $\Delta T = (Tm° - T_C)$.

In Figure 3 it is possible to observe that for PET-1 and 2 the crystallization rate (proportional to ln K) increases as the molecular weight decreases, as expected for the polymer crystallization controlled by kinetic effects. For PET-I1, instead, the crystallization rate is very similar to that of PET-1, which has a higher molecular weight, i.e. PET-I1 crystallizes more slowly than that expected for a PET sample which the same intrinsic viscosity. This results is interpreted by the effect of the ionic aggregations present in the melt, that decrease the mobility of the chains, as observed by melt rheology analyses18). It is interesting to observe that PET-I1 is characterized by a very low content of ionic groups (0.6 mol%), suggesting that the presence of sulfonated units at the chain ends induces very significant effects.

The comparison between the crystallization rates of ionomers at different degrees of sulfonation emphasizes this trend: the crystallization rate results strongly dependent on the ionic content more than on the molecular weight.

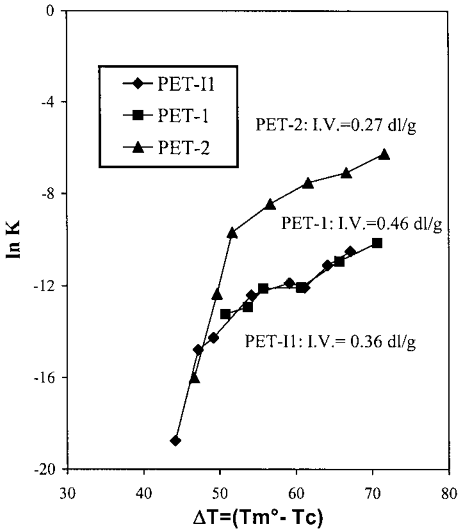


Fig. 3: Avrami constant as a function of the undercooling for two PET homopolymers and a PET-ionomer.

Conclusion

A new route of synthesis of ionomers is proposed, based on the reactive blending in Brabender between PET and a sulfonated ester: transesterification reactions occur in the melt, leading to a decrement of molecular weight and the insertion of ionic groups at the chain ends. However, the insertion of 2-SBABE is not complete, suggesting that the presence of sulfonated groups modifies the reactivity of ester groups.

A small quantity of sulfonated groups as chain ends is enough to induce important modifications in the thermal properties of the ionomers, in terms of thermal stability, equilibrium melting temperature and crystallization rate. These results are interpreted by the formation of strong associations between ions in the solid state and in the melt. Therefore, differently from the random ionomers, where the formation of a three-dimensional network may place some restrictions on the self-association process, in halato-telechelic ionomers the polymer chains do not interfere with the dipole association and the modification of the properties is very significant also at low level of ionic content.

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