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Hydrolytic stability of sulfonated poly(butylene terephthalate)

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Abstract

The hydrolysis of sulfonated poly(butylene terephthalate) copolymers was studied. Sulfonated poly(butylene terephthalate) copolymers, referred to as PBT-ionomers (PBTIs), were shown to hydrolyze faster than poly(butylene terephthalate) (PBT). An experiment designed to isolate the effect of the sulfonated isophthalate (SIP) moieties on hydrolysis rate showed that the SIP moieties were responsible for the faster hydrolysis. Experiments aimed at identifying the mechanism of influence of the SIP moieties on hydrolytic stability indicated that hydrolysis was enhanced by the presence of ionic multiplets which increase amorphous content, imbibe water, and perhaps exert a medium effect on the hydrolysis of esters associated with the ionic groups.

Keywords: Hydrolytic stability; Poly(butylene terephthalate); Hydrolysis

1. Introduction

Poly(1,4-butylene terephthalate) (PBT) has become a very important semicrystalline thermoplastic for injection-molding applications. The strengths of PBT as an engineering thermoplastic resin are excellent melt processability, fast crystallization, and good mechanical properties. One of the inherent shortcomings of PBT, due to its polyester backbone, is its susceptibility to hydrolytic degradation [1,2].

Our search for new materials with unique physical properties led us to study the modification of PBT by sodium sulfonate groups (Fig. 1). The level of sodium sulfonate groups of the copolymers of interest was less than 10 mol%. Therefore, they were considered members of the class of polymers referred to as ionomers [3]. For this class of materials, it is well known that the ion pairs in an ionomer aggregate together to form quadruplets, sextuplets, and higher aggregates, collectively called multiplets [4]. Aggregate size and the number of ions per aggregate depend on the nature of both the anion and cation and the chemical composition of the polymer matrix. In general, the number of ions per aggregate decreases with increasing matrix polarity for a given ion pair composition.

It has been shown by many investigators that the presence of ionic functionality in polymers can have dramatic effects on polymer properties such as melt viscosity, crystallization rate, toughness, and solubility [5]. While considerable effort has gone into the study of semicrystalline ionomers such as polyethylene ionomers [5] and syndiotactic polystyrene ionomers [6,7], very little work has been reported on the properties of PBT-ionomers (PBTIs) [8,9]. The earliest investigation of PBTIs was that of Gorda and Peiffer in 1992 [10]. These investigators studied the effect of the sodium sulfonate group on the morphology and mechanical properties of PBTIs by comparing results to analogous PBT copolymers containing isophthalate comonomer units. The results of the study showed that the sulfonate groups retard the crystallization process and improve mechanical properties suggesting the presence of ionic multiplets in PBTIs. Ostrowska-Czubenko and Ostrowska-Gumkowska have provided evidence of ionic aggregation in PETIs using far-infrared analysis [11] and thermal analysis [12]. Due to the inherent susceptibility of PBT to hydrolytic degradation, we were interested in understanding the effect the presence of the sodium sulfonate-containing comonomer would have on hydrolytic stability.

A literature survey on the topic of sulfonate-containing polyesters revealed several reports pertaining to the

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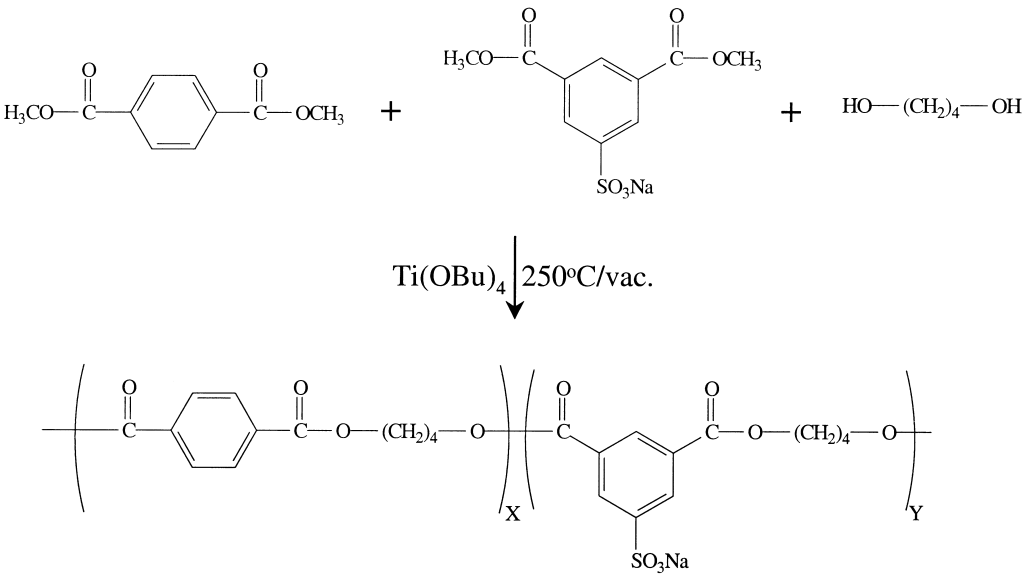

Fig. 1. The synthesis of sulfonated poly(butylene terephthalate) copolymers (PBT-ionomers).

hydrolytic stability of poly(ethylene terephthalate) copolymers containing the sodium sulfonate functionality (PETIs). The interest in PETIs stems from the commercial utility of these copolymers in the textile industry for their excellent dyeability with cationic dyes. All of the publications concerning the hydrolytic stability of PETIs indicated that the hydrolysis rate of PETIs were faster than PET [13–17]. While agreement existed with regard to the reduced hydrolytic stability of PETIs as compared to PET, the rationale for the difference in hydrolytic stability varied between investigators.

Grobe et al. [13], based on hydrolysis rates determined for bis(2-hydroxyethyl)terephthalate and sodium-3,5-bis[(2-hydroxyethoxy)carbonyl]benzenesulfonate in an aqueous alkaline solution, concluded that the sodium sulfonate functionality had no catalytic or inductive effect on hydrolysis since the saponification rates of the two model compounds were essentially equivalent. These authors attributed the faster hydrolysis of PETIs to the *meta* position of the ester linkages associated with the sulfonated isophthalate (SIP) moieties which facilitated the diffusion of hydroxide ion into the bulk of the sample and increased the accessibility of the ester linkages.

Datye and Palan [14] proposed that the faster saponification of PETIs compared to PET was due to the greater hydrophilicity of the former which facilitated the transport of hydroxide ions to the ester linkages. Burget et al. [15] studied the hydrolysis of PETI fibers immersed in an aqueous solution at pH 2.8 and temperature of 130 °C. They proposed that the faster hydrolysis of PETI as compared to PET was due to an exchange between sodium ions of the PETI sulfonate groups with protons from the bath to produce sulfonic acid groups capable of strongly catalyzing hydrolysis.

No reports were found concerning the hydrolysis of polyester-ionomers under essentially neutral conditions or conditions in which the only catalyst for hydrolysis was the polymer's own carboxylic acid endgroups. The purpose of the research described in this paper was to determine the effect of the sodium sulfonate comonomer units on the hydrolytic stability of PBTIs and to understand the mechanism of influence of these units on hydrolysis of the polymer chain.

2. Experimental

2.1. Materials

The PBTI sample used for the investigation was produced by the melt copolymerization of dimethylterephthalate (DMT), 1,4-butanediol (BD), and dimethyl-5-sodiosulfoisophthalate (DMSIP), as shown in Fig. 1. A description of the synthesis is as follows: 125.9 lb of DMT, 5.94 lb of DMSIP, 100.1 lb of BD, and 43 ml of tetraisopropyl titanate were charged to a 40CV Helicone reactor which was preheated to 130 °C. The monomer mixture was then heated to 225 °C at a rate of 1.5 °C/min under atmospheric pressure and most of the methanol by-product removed by distillation. The mixture was then subjected to a gradual reduction in pressure at a rate of 20 mm Hg/min while the temperature was simultaneously increased to 250 °C at a rate of 1.5 °C/min. After 210 min under vacuum, the polymer was released from the reactor and chopped into granules. The melt viscosity of the PBTI measured at 250 °C and a shear rate of 100 s^{-1} was 11,100 poise. The number-average molecular weight (M_n) was 15,000 g/mol and the carboxylic acid (COOH) and hydroxyl endgroup (OH) concentration was 42 and 91 meq/kg, respectively. The PBTI samples used to determine the effect of the $-SO_3Na$

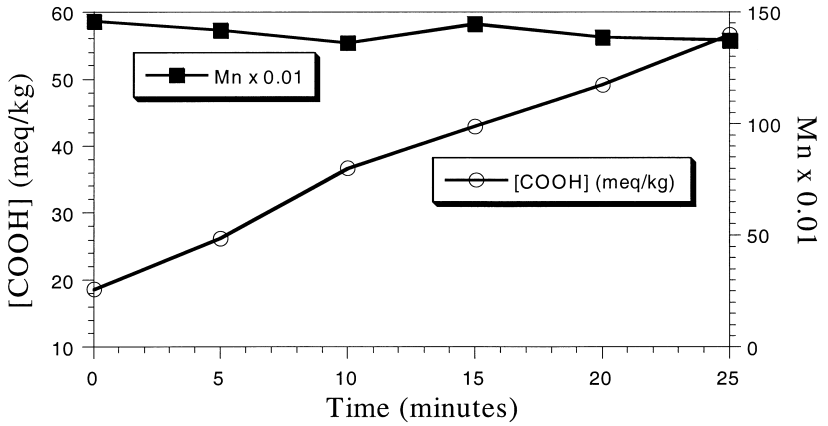

Fig. 2. The change in PBT-COOH endgroup concentration and molecular weight as a function of aging time in the melt at 250 °C.

groups on crystallizability were produced in a similar fashion as described above with the exception that DMSIP concentration was varied.

The PBT utilized was Valox®195 from GE Plastic and 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (ERL) was ERL4221 from Union Carbide Corporation. Sodium stearate and sodium benzene sulfonate (NaBS) were used as received from Aldrich Chemical. Acetone, *o*-dichlorobenzene (ODCB), hexane, and methylene chloride were used as received from J.T. Baker. DMT was obtained from Kosa Corporation; while BD and DMSIP were obtained from BASF and DuPont, respectively.

2.1.1. Synthesis of PBTI and PBT model polymers containing no COOH endgroups

As stated above, the PBTI sample utilized had a COOH concentration ([COOH]) of 42 meq/kg and an M_n of about 15,000 g/mol. It was important that the PBT used for the experiment be chemically equivalent to the PBTI with the exception, of course, to the presence of the SIP moiety. Thus, a PBT sample was needed that had a [COOH] of approximately 40 meq/kg and an M_n of approximately 15,000 g/mol.

VALOX®195 is a commercial PBT from GE Plastics that has an M_n of about 15,000 g/mol and a [COOH] of about 20 meq/kg. This material was converted to the desired PBT sample by melt aging the material at 250 °C to take advantage of the prominent side reaction that occurs for PBT involving the conversion of a hydroxyl endgroup to a COOH endgroup by an intramolecular cyclization reaction resulting in the formation of a molecule of tetrahydrofuran [18]. Fig. 2 shows the change in [COOH] with aging time at 250 °C. Melt aging was done in the barrel of a capillary rheometer, and [COOH] was measured by titration. From this data, it was determined that a melt aging time of 15 min could be used to produce the PBT sample desired. Thus, about 100 g of PBT possessing a [COOH] of approximately 40 meq/kg and an M_n of about 15,000 g/mol was made by doing four melt aging runs (25 g of PBT per run) in a capillary rheometer at 250 °C for 15 min. The strands of PBT from the four batches were cut into small pieces and mixed together by shaking in a plastic bag. The entire sample was then cryogenically ground into a powder and the endgroup composition determined on the powder sample. The [COOH] was 40 meq/kg and the M_n was 14,800 g/mol.

Reaction of the COOH endgroups with ERL was done in refluxing ODCB using a 20-fold excess of ERL relative to [COOH]. The procedure was as follows: 480 ml of ODCB was heated to reflux in a 1000 ml three-neck, round-bottomed flask equipped with an overhead stirrer, condenser, and heating mantle. Upon reflux, 60 g of the ground PBTI was added to the flask. After dissolution, approximately 200 ml of ODCB was distilled from the flask to remove water from the system. Next, 0.24 g of sodium stearate was added to the refluxing solution and after 5 min, a 50% solution containing 12 g of ERL in ODCB was quickly added. After 30 min of reaction time, the hot solution was slowly poured into rapidly stirred hexane. The precipitated polymer was isolated by vacuum filtration and washed extensively with methylene chloride. The precipitate was then vacuum dried to remove residual methylene chloride.

2.1.2. Production of the PBT/NaBS blend

Since NaBS was a crystalline powder with a melting point above 300 °C, it was necessary to utilize a melt extrusion process to incorporate the NaBS into the PBT matrix. As a result, it was decided to use the extrusion process to all but eliminate the COOH endgroups by reaction with ERL in the melt.

The PBT/NaBS pre-extrusion mixture was produced by stirring 144.47 g of VALOX®195 pellets, 5.53 g of NaBS, 2.25 g ERL, and 0.105 g sodium stearate together in a polyethylene beaker using a spatula. The mixture was then extruded on a PRISM 16 mm twin screw extruder using barrel temperature settings of 255 °C and a screw speed of 150 rpm. A control sample was produced in analogous fashion with the exception that the NaBS was left out and 150.00 g of VALOX®195 was used. The COOH endgroup concentration and residual epoxide concentration as

measured by potentiometric and colorimetric titration, respectively, were very similar for the two materials. The PBT/NaBS sample was found to possess a [COOH] of 3.4 meq/kg and an epoxide concentration of 115 meq/kg, while the PBT control sample possessed a [COOH] and epoxide concentration of 6.0 and 113 meq/kg, respectively.

2.2. Characterization

[COOH] was determined by potentiometric titration using an APB 410 automated titration system from Kyoto Electronics. About 0.5–1.5 g of polymer was dissolved in about 20 ml of hot *o*-cresol. Once dissolved, the solution was allowed to cool to room temperature and then about 50 ml of methylene chloride was added. The solution was titrated with 0.01N tetrabutylammonium hydroxide and the [COOH] expressed in milliequivalents per kilogram (meq/kg).

[OH] was determined using a modification of the method described by Kosky et al. [19]. The modification to the procedure involved the use of an internal overtone peak for normalization of the sample thickness. The ratio of the absorptions of the hydroxyl group to the overtone peak was then referenced to ^{1}H-NMR measurements of the absolute concentration to generate a standard curve.

Number-average molecular weight was calculated from [COOH] and [OH] and the knowledge that essentially all the polymer endgroups are either COOH or OH. Residual epoxide content was determined using a modification of ASTM D 1652-88. The modification involved the use of a 60/40 w/w mixture of phenol and 1,1,2,2-tetrachloroethane to dissolve the polymer.

Thermal properties were determined by differential scanning calorimetry (DSC) using a Perkin Elmer DSC7. Crystallization temperature was reported as the minimum in the crystallization exotherm produced by cooling 3.0–4.5 mg specimens from the melt. The exact heating and cooling profile used was: (1) heat from 30 to 265 °C at 40 °C/min; (2) hold at 265 °C for 4.0 min; (3) cool from 265 to 30 °C at 40 °C/min; (4) hold at 30 °C for 4.0 min; (5) heat from 30 to 250 °C at 40 °C/min. In addition to measuring the peak crystallization temperature, the heat of crystallization was measured by integrating the area of the crystallization exotherm. The crystallization temperatures and heats of crystallization reported in this paper were all averages of three measurements.

2.3. Model compound study

The model compound study was done by first preparing 60/40 acetone/water v/v stock solutions of 0.05 M DMT, 0.05 M DMSIP, and 0.05 M DMT with 1.615×10^{-3} M NaBS, respectively. The solutions were prepared at 40 °C to maintain solubility of DMT. An Eppendorf pipette was used to transfer 0.70 ml aliquots of a stock solution to a reaction vessel. The reaction vessels were 0.25 in. stainless steel Swagelok® bulkhead unions with plugs. The temperature of the stock solutions were maintained at 40 °C during the transfer to the reaction vessels. The filled and sealed reaction vessels were placed in 100 ml beakers with about seven reactors per beaker and the beakers submerged in an evaporating dish filled with silicone oil. The silicone oil was heated to 105 °C over a 15 min period. In addition to the DMT, DMSIP, and DMT/NaBS samples, reaction vessels were added that only contained solvent for use as solvent blanks for titration. Samples were removed from the oil bath with time and each reaction mixture diluted with approximately 40 ml of deionized water and potentiometrically titrated with 0.002 M aqueous sodium hydroxide. Thus, one reaction vessel was used to produce one data point in Fig. 5.

2.4. Procedure for determining the hydrolytic stability of polymer samples

The hydrolytic stability of polymer samples was determined by first compression molding discs 25.0 mm in diameter and about 1.5 mm thick. A set of discs were then placed in an autoclave and samples removed with time. The autoclave was an Amsco model 3031 autoclave and the temperature and pressure were 120 °C and 17 psi, respectively. The degree of hydrolytic degradation was monitored by measuring [COOH] of the polymer since each hydrolysis event results in the generation of a COOH endgroup.

3. Results and discussion

As stated previously, the purpose of the research described in this paper was to determine the effect the sodium sulfonate comonomer (SIP) units have on the hydrolytic stability of PBTIs and to understand the mechanism of influence of these units on hydrolysis. Isolation of the effect of the SIP units was accomplished by: (1) synthesizing a PBTI and PBT sample with the same M_n and the same endgroup composition ($[COOH]_{PBTI} = [COOH]_{PBT}$); (2) removing the influence of COOH endgroups on hydrolytic stability by essentially completely reacting them with ERL; and (3) comparing the hydrolytic stability of the purified materials. The rationale for removing the influence of the COOH endgroups on hydrolytic stability by reacting them with an epoxide stems from the knowledge that COOH endgroups catalyze hydrolysis [20].

As shown in Fig. 3, the PBTI sample generated COOH endgroups much faster than the PBT sample when subjected to autoclave conditions of 120 °C and 17 psi pressure. This result clearly showed that PBTI, due exclusively to the presence of the SIP moieties, was inherently more susceptible to hydrolytic degradation than PBT.

Some possible mechanisms of hydrolytic destabilization by the SIP moieties are as follows:

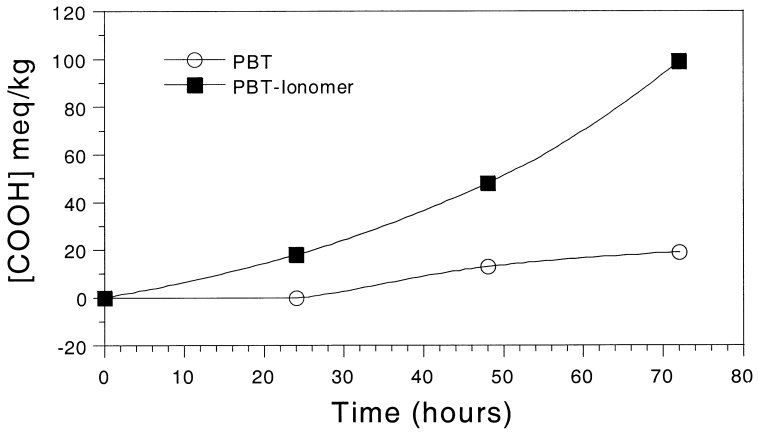

Fig. 3. The hydrolytic stability of fully COOH capped PBT-ionomer as compared to an equivalent fully COOH capped PBT.

1. *SIP ester reactivity*: the ester linkages of the SIP comonomer units may be more reactive toward hydrolysis than the ester linkages of the PBT monomer units due to an inductive effect by $-SO_3Na$ and/or *meta* positioning of the ester groups;
2. *Water concentration effect*: due to greater hydrophilicity and lower crystallinity, the water concentration within PBTI may be higher than PBT resulting in faster hydrolysis of PBTI;
3. *Medium effect*: the local environment of the ionic aggregates may be more conducive to hydrolysis due to higher polarity and the ionic character of the aggregates;
4. *Catalytic effect by* $-SO_3Na$: although a very weak base, $-SO_3Na$ may serve as a catalyst for hydrolysis; and/or
5. *Catalytic effect by* $-SO_3H$ *impurities*: sulfonic acid impurities entrained in the polymer may be serving as a catalyst for hydrolysis.

Several experiments were conducted to try to probe some of these hypothetical mechanisms. In order to separate the effect of SIP ester reactivity (mechanism 1) from the other possible mechanisms, the hydrolytic stability of a PBT sample possessing a very low [COOH] (~3 meq/kg), due to reaction with ERL, was compared to an analogous PBT sample containing 3.69 wt% NaBS. This level of NaBS provides the same concentration of sodium sulfonate groups in the material as found in the PBTI model polymer.

As shown in Fig. 4, the presence of NaBS significantly enhanced the rate of hydrolysis. This result indicated that the faster hydrolysis rate of PBTI was not due solely to a faster rate of hydrolysis of SIP esters versus PBT esters (mechanism 1). The aromatic sodium sulfonate group itself, enhanced the rate of PBT ester hydrolysis perhaps by one or a combination of a catalytic (mechanisms 4 or 5), medium (mechanism 3), or water concentration effect (mechanism 2).

To directly probe and quantify the contribution of SIP ester reactivity to the rate of hydrolysis of PBTI as well as to eliminate water concentration as a variable in the comparison of rates of hydrolysis, a model compound study was conducted. DMT and DMSIP were used as model compounds for PBT ester groups and SIP ester groups, respectively. The hydrolysis rates of DMT, DMSIP, and DMT in the presence of NaBS (97/3 mol/mol DMT/NaBS) were determined in 60/40 acetone/water at 105 °C. As shown in Fig. 5, the hydrolysis followed pseudo-first order kinetics for all three compositions. Using this data, it was concluded that the hydrolysis rates of DMT, DMSIP, and

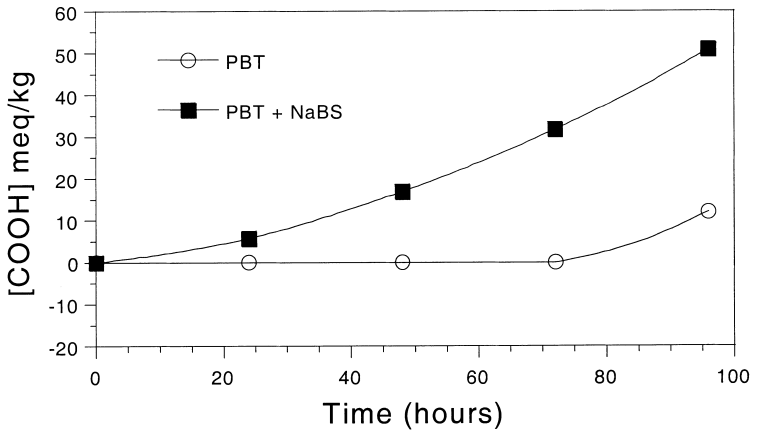

Fig. 4. The effect of the presence of sodium benzene sulfonate (NaBS) on the hydrolytic stability of fully COOH capped PBT.

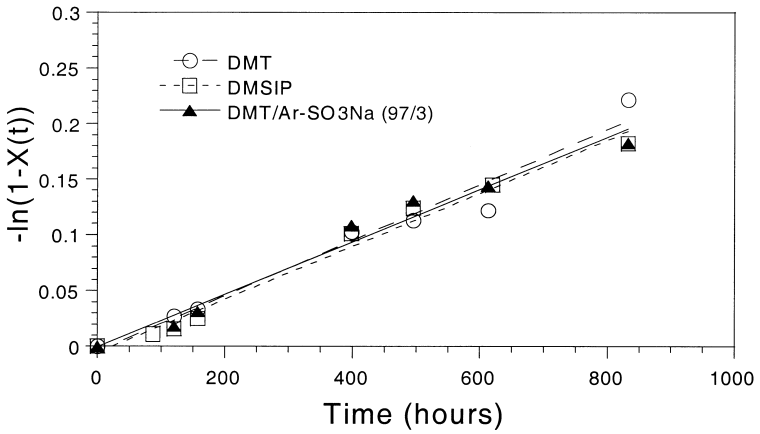

Fig. 5. Psuedo-first order kinetic plots for the hydrolysis of DMT, DMSIP, and DMT in the presence of NaBS (97/3 mol/mol DMT/NaBS).

DMT in the presence of 3.0 mol% NaBS were essentially equivalent, within experimental error.

The results obtained for the hydrolysis of DMT and DMSIP suggest that the inductive effect induced by a *meta*-SO_3Na group together with a *meta*-CO_2CH_3 group is approximately equivalent to that of a *para*-CO_2CH_3 group for the hydrolysis of methyl benzoate. The Hammett substituent constant for a *meta*-SO_3^-, *meta*-CO_2CH_3, and *para*-CO_2CH_3 is 0.05, 0.32, and 0.39, respectively [21]. Based on these substituent constants and the fact that alkyl benzoate hydrolysis is quite susceptible to substituent effects (ρ for acid-catalyzed hydrolysis of ethyl benzoate is 2.146), it is not surprising that the hydrolysis rate of DMSIP was similar to that of DMT.

The fact that the hydrolysis rate of DMT was unaffected by the presence of NaBS indicated that the aromatic –SO_3Na group does not serve as a catalyst for the hydrolysis, at least not in the soluble state.

Since DMSIP did not hydrolyze faster than DMT, it seemed unlikely that possible sulfonic acid impurities present in DMSIP was the fundamental cause of the poor hydrolytic stability of PBTI (mechanism 5). None-the-less, DMSIP was titrated with base to measure the amount of acid impurities. Two titration endpoints were observed which were attributed to the presence of both carboxylic acid impurities and sulfonic acid impurities. The concentration of the sulfonic acid impurity and carboxylic acid impurity was 5 and 2 meq/kg, respectively. The carboxylic acid impurity was most likely the result of incomplete esterification of sulfonated isophthalic acid with methanol during the production of DMSIP. Since the amount of DMSIP used to produce the PBTI was 3.0 mol% relative to DMT, the maximum amount of sulfonic acid impurity that would have been entrained in PBTI would have been 0.15 meq/kg. Since sulfonic acids are not thermally stable, it was unlikely that the residual sulfonic acid would have survived the polymerization process without being decomposed [22]. Further, the sodium stearate used to catalyze the COOH/ERL reaction during extrusion was at a 15-fold excess to the residual sulfonic acid and therefore would result in neutralization of the impurity. Due to these considerations, 'mechanism 5' was ruled out as a fundamental cause of the poor hydrolytic stability of PBTI.

The results of the model compound study showed that SIP ester groups were essentially no more or less reactive towards water than PBT ester groups. In addition, no catalytic effect by –SO_3Na or acid impurities in DMSIP was found. Thus, it appeared that the faster rate of hydrolysis of PBTI relative to PBT was due to the change in solid-state characteristics of the material caused by the presence of the SIP comonomer units.

The SIP comonomer units, due to the 1,3-ester linkages and presence of the –SO_3Na group, cannot be incorporated into the crystalline lattice with butylene terephthalate repeat units. As a result, for a given thermal history, the crystallinity of PBTI would be lower than PBT. This characteristic of PBTI was observed by determining the crystallization temperature (T_c) and heat of crystallization (ΔH_c) of PBTI as a function of —SO_3Na content using controlled cooling from the melt by DSC [23]. Table 1 contains the data obtained from the DSC experiment which clearly demonstrates the crystallization inhibiting effect of the SIP comonomer units. This behavior has also been observed by Gorda and Peiffer [10] for PBTI and Guo et al. for PETI [24].

The higher amorphous content of PBTI as compared to PBT would be expected to result in greater water uptake and, thus, faster hydrolysis during hydrolytic stability testing since the temperature used for the testing was above the T_g of the polymer. The higher water uptake was

Table 1
T_c and ΔH_c data obtained as a function of –SO_3Na content. All polymers possessed a number average molecular weight of about 15,000 g/mol

–SO_3Na (mol%)	T_c (°C)	ΔH_c
0	182.0	−50.5
1	178.5	−47.6
3	170.0	−46.5
5	160.3	−44.9

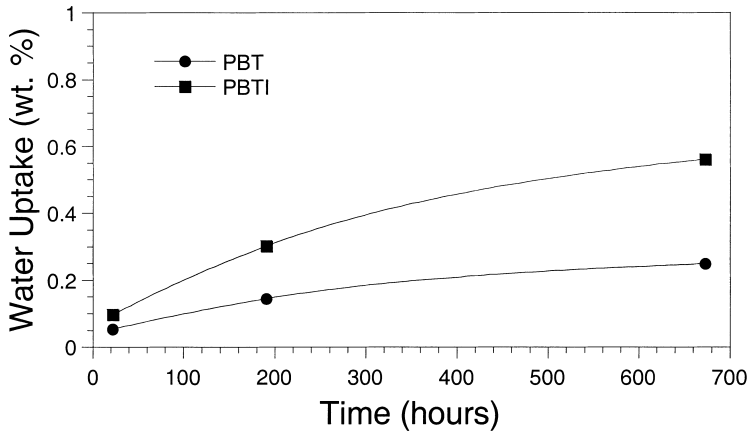

Fig. 6. Water uptake after immersion at 22 °C for PBT and PBTI containing 3 mol% SIP units.

illustrated by immersion of molded samples in water at room temperature (Fig. 6). A PBTI containing 3.0 mol% sodium sulfonate groups took up twice as much water by weight than PBT.

While an increased amorphous content would be expected to result in faster hydrolysis, this was not the only factor which resulted in faster hydrolysis of PBTI relative to PBT. As shown in Fig. 4, the addition of NBS to PBT resulted in an increase in the rate of hydrolysis even though the crystallizability of this sample, as determined by DSC experiments, was essentially the same as pure PBT. Thus, the presence of the $-SO_3Na$ groups produces an additional increase in hydrolysis rate above and beyond that which would be expected based on the existence of a higher amorphous content relative to pure PBT. Due to the ionic and hydrophilic nature of the ionic multiplets, they possess a very different local chemical environment than the non-ionic 'matrix' of the material.

Due to the high polarity and ionic nature of the sodium sulfonate groups, the hydrolysis rate of ester groups in the vicinity of the ionic multiplets may be increased due to one or a combination of the following factors involving coordination or interaction with sodium sulfonate groups: (1) an increase in the ground state energy of reactants by greater polarization of water molecules and/or ester carbonyls; (2) a decrease in transition state energy by greater stabilization of the activated complex; or (3) an enhancement in the rate of proton transfer.

Based on previous work by Vanhoorne and Register [25] as well as Chisholm et al. [23], it was believed that COOH endgroups of PBTI interact directly with the ionic multiplets. As a result, the presence of COOH endgroups would result in faster hydrolysis of ester groups in the vicinity of the ionic multiplets as compared to those in the non-ionic matrix.

4. Conclusion

The work described in this paper has clearly shown that PBTI hydrolyzes faster than PBT as expected based on previous reports for similar polyester ionomers. The role of the SIP group was demonstrated through a series of experiments aimed at isolating that effect from other possibilities. Experimental work was carried out to elucidate the mechanism of the rate enhancement resulting from the presence of the sulfonate groups. The results of the mechanistic studies can best be interpreted by postulating that the presence of the ionic groups leads to higher water absorption in PBTI than PBT. This increase was verified experimentally. The higher water absorption was due to an increase in the amorphous content of the material resulting from the crystallization retarding effects of the SIP comonomer units and the higher hydrophilicity of the polymer. In addition, the high polarity and ionic nature of the sodium sulfonate groups may increase the hydrolysis rate of ester groups associated with the ionic multiplets by a medium effect involving coordination or interaction of reactants and/or transition state species with sodium sulfonate groups.

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