

# Rheological Behavior of Poly(1,4-butylene isophthalate) Containing Sodium Sulfonate Groups

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## SYNOPSIS

The steady-state rheological behavior in the melt of poly(1,4-butylene isophthalate)s containing various amounts of sodium sulfonate groups has been investigated using a capillary rheometer. It has been found that the presence of SO<sub>3</sub>Na groups strongly enhances the melt viscosity and this result cannot be explained as due to the small increase of the glass transition temperature, but has to be attributed to the relevant interactions between ionic groups. Measurements carried out at different temperatures in the range 190–220°C have shown that the “Newtonian” viscosity of sulfonated poly(1,4-butylene isophthalate) is well correlated to temperature by an Arrhenius-type equation. The activation energy for melt flow has been found to increase linearly with SO<sub>3</sub>Na group content in the polymer. Furthermore, it has been found that for samples having a content of ionic groups of 5% or higher and a sufficiently high molecular weight the time–temperature superposition principle does not hold. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

For many years 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 result in physical thermolabile cross-linking.<sup>1–5</sup>

Polymers containing up to 10–15 mol % of ionic groups are commonly called ionomers, whereas the term polyelectrolytes is applied in the case of greater ionic amounts. In general, polyelectrolytes have some specific applications, whereas ionomers, depending on the nature of the nonionic backbone and on the kind and concentration of ionic groups, have been proposed to substitute for nonionic polymers in many different fields, from that of flexible plastics to vulcanized rubbers, showing a wide range of in-

teresting properties, such as high abrasion resistance and high melt strength.

It has to be emphasized that the presence of ionic groups causes significant modifications of the rheological behavior of polymers, in particular, a marked increase of the melt viscosity and of the activation energy for melt flow. Most of the previous studies on the melt rheology of linear ionomers refer to ethylene<sup>6,7</sup>-, propylene<sup>8</sup>-, EPDM<sup>9,10</sup>- and styrene<sup>11,12</sup>-based ionomers and little attention has been devoted up to now to polyester ionomers.<sup>13,14</sup>

In the present article, the results of a detailed investigation on the steady-state rheological behavior of copolyesters derived from isophthalic acid and containing various amounts of sodium sulfonate groups are reported.

## EXPERIMENTAL

### Synthesis of Polymer Samples

Reagent-grade dimethylisophthalate (DMIP), dimethyl 5-sulfoisophthalate sodium salt (DMSIP), and 1,4-butanediol (BD) were used as supplied by

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Aldrich; titanium tetrabutoxide (Aldrich) was distilled at reduced pressure before use.

A 1.8 L stainless-steel batch reactor was used for polymerization, which was 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. Poly(butylene isophthalate-*co*-butylene sulfoisophthalate) (PBSIP) samples were obtained by the usual two-stage equilibrium polycondensation, starting from DMIP, DMSIP, and BD with  $\text{Ti}(\text{OBU})_4$  as catalyst, employing molar ratios DMSIP/DMIP ranging from 2% to about 15% to obtain copolymers with different compositions. For each polymerization reaction, several samples were taken from the bottom of the reactor at different reaction times to obtain samples with the same composition and different molecular weights. Additional details on the polymerization conditions are reported elsewhere.<sup>15</sup>

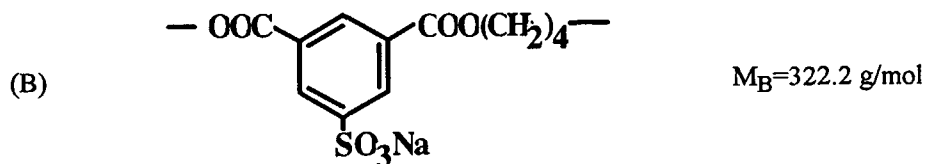
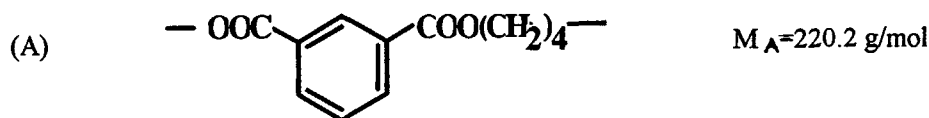
### Molecular Weight Determination

Number-average,  $M_n$ , and weight-average,  $M_w$ , molecular weights were calculated for each sample from the content of terminal functional groups (hydroxyl and carboxyl groups). The carboxyl group content was determined by direct titration, and the hydroxyl one, by spectrophotometric methods, as reported previously.<sup>15</sup>

The reaction conversion  $p$  was calculated by the equation

$$p = 1 - \frac{E}{2} (M_A X_A + M_B X_B) \quad (1)$$

where  $E$  is the number of total end groups in equivalents/(gram of polymer),  $M_A$  and  $M_B$  are the molecular weights of the monomeric units of two kinds:



and  $X_A$  and  $X_B$  are the molar fractions of isophthalate and sulfoisophthalate units in the copolymer.

The number-average molecular weight,  $M_n$ , was calculated, neglecting the presence of cyclic molecules, using the following equation:

$$M_n = \frac{M_{n,0}}{1 - p} \quad (2)$$

where  $M_{n,0}$ , the number-average molecular weight of the repeating unit, is given by:

$$M_{n,0} = X_A M_A + X_B M_B$$

The weight-average molecular weight,  $M_w$ , was calculated with the further assumption that the distributions of molecular weights and of composition are the "most probable" because of the reaction

conditions employed, i.e., high temperature and  $\text{Ti}(\text{OBU})_4$  as the catalyst.

Under these conditions,  $M_w$  is given by<sup>16</sup>

$$M_w = M_{w,0} + \frac{2pM_{n,0}}{1 - p} \quad (3)$$

where

$$M_{w,0} = W_A M_A + W_B M_B$$

$W_A$  and  $W_B$  being the weight fractions of the monomeric units of the two kinds in the copolymers.

### Sulfonate Group Analysis

The content of sulfonate groups was determined both by means of an oxygen flask combustion procedure (according to Schöniger method) and of an ion-exchange treatment, as described previously.<sup>15</sup>

## Rheological Measurements

The melt viscosities of the copolymer samples were measured at various shear rates using a Rheoscope 1000 (CEAST) capillary rheometer. The instrument is basically an electrically thermostated stainless-steel barrel in the bottom of which one of a number of interchangeable capillaries can be inserted. The polymer melt is forced through the capillary at pre-selected constant rates by a plunger; the force necessary to drive it at a fixed speed is measured by a compression load cell. The capillary used had a nominal inner diameter of 1.00 mm, a length-to-diameter ratio  $L/D$  of 40, and an entrance angle of  $90^\circ$ .

The tests were carried out in the temperature range  $190$ – $230^\circ\text{C}$ , for a period of time of  $15$ – $20$  min; under these conditions, the samples were thermally stable. Before testing, the polymer samples were dried under vacuum at  $90^\circ\text{C}$  for about  $24$  h.

The apparent Newtonian shear rate at the wall,

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3} \quad (4)$$

(where  $Q$  is the volumetric flow rate and  $R$  is the capillary radius) was calculated and corrected by means of the well-known Rabinowitsch procedure<sup>17</sup> to take into account the non-Newtonian behavior of the polymer and to obtain the true shear rate at the wall:

$$\dot{\gamma} = \frac{3n' + 1}{4n'} \dot{\gamma}_a \quad (5)$$

( $n'$  being defined as the slope of a log–log plot of the wall shear stress  $\tau = PR/2L$  vs.  $\dot{\gamma}_a$ ). In this procedure, the assumptions are that there is no slip at the wall and that the entrance effects can be neglected. Finally, the viscosity was obtained as the ratio between the shear stress and the shear rate at the wall:

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (6)$$

## RESULTS AND DISCUSSION

The basic parameters from which the rheological properties of polymers are influenced are the chemical structure and composition, the glass-transition temperature,  $T_g$ , as referred to the measurement temperature  $T$ , and the molecular weight. As far as the ionomeric polymers are concerned, strong effects on viscosity of the ionic group and of their concentration are expected.

The samples here investigated are linear ionomers, whose weight-average molecular weight ranges from  $14,000$  to  $40,000$  and whose melting temperature falls between  $130$  and  $140^\circ\text{C}$ , i.e.,  $50^\circ\text{C}$  or more

**Table I** Characterization Data of PBSIP Samples

Sample	SO <sub>3</sub> Na Group Content (mol %) <sup>a</sup>	$M_w \times 10^{-4}$ <sup>b</sup>	$T_g$ ( $^\circ\text{C}$ ) <sup>c</sup>	$T_m$ ( $^\circ\text{C}$ ) <sup>c</sup>	$\eta_0$ (Pa s) <sup>d</sup>	$E_0$ (kcal/mol)
A1	2.4	2.33	22.8	141.8	74	16.8
A2	2.4	3.12	—	—	184	16.0
A3	2.4	3.96	—	—	1100 <sup>e</sup>	17.5
B1	5.1	1.98	23.7	137.3	120	18.4
B2	5.1	2.51	—	—	318	18.5
B3	5.1	3.36	—	—	4300 <sup>e</sup>	20.0
C'1	9.1	1.92	25.9	128.1	215	19.2
C'2	9.1	2.23	—	—	580	20.9
C'3	9.1	3.14	—	—	4500 <sup>e</sup>	21.1
D1	15.4	1.50	—	—	330	24.3
D2	15.4	1.71	—	—	1100	25.8
D3	15.4	1.80	—	—	1200	26.4
D'1	15.3	1.37	—	—	240	22.9
D'2	15.3	1.81	32.0	—	1050	24.8

<sup>a</sup> Calculated from sulfur analysis results.<sup>15</sup>

<sup>b</sup> Calculated with eq. (3) from the total content of end groups.

<sup>c</sup> From Ref. 15.

<sup>d</sup> At  $200^\circ\text{C}$ .

<sup>e</sup> Extrapolated value.

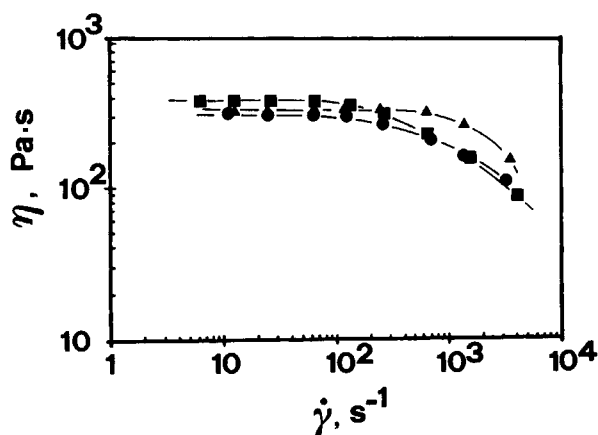
below the rheological measurement temperatures. As far as the glass transition temperature is concerned,  $T_g$  was found to vary between 23 and 32°C, depending on ionic groups concentration and thermal history of the sample.<sup>15</sup> Characterization data are collected in Table I.

Typical viscosity–shear rate curves at the temperature of 200°C are reported in Figures 1 and 2, as a representation of samples with different ionic content having, respectively, similar viscosity and similar molecular weight. The influence of the concentration of ionic groups on viscosity is seen to be rather strong, but, nevertheless, when the curves are normalized with respect to the zero-shear “Newtonian” viscosity,  $\eta_0$ , i.e., when the ratio  $\eta/\eta_0$  is plotted as a function of a “reduced” shear rate  $\dot{\gamma}\tau_\eta$  (where  $\tau_\eta$  is an adjustable experimental time), one finds, as shown in Figure 3, that a general “master curve” is applicable to all the data, including those concerning poly(butylene isophthalate) (PBIP) reported previously.<sup>18</sup> As a conclusion, one is led to believe that the presence of ionic groups in the polymer melt does not modify appreciably the mechanism of flow, since the flow curves belong to the same type.

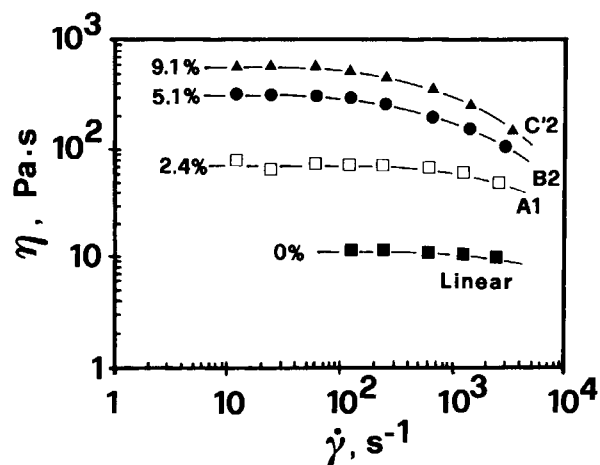
For nonionic linear polymers, the “Newtonian” viscosity is a function of molecular weight, given by the equation

$$\eta_0 = KM_w^{3.4} \quad (7)$$

For the ionomeric samples investigated here, the plot of  $\eta_0$  vs.  $M_w$  is shown in Figure 4. Although limited data are available for each composition, it is clear that the Newtonian viscosity  $\eta_0$  is strongly increased by the ionic group content. Moreover, the slope of



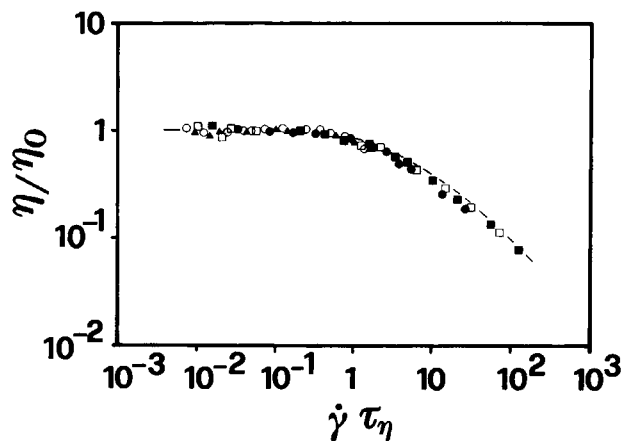
**Figure 1** Melt viscosity vs. shear rate at 200°C for PBIP and PBSIP samples exhibiting about the same  $\eta_0$  but having different sulfonate group content and different  $M_w$ : (■) PBIP L7 (from Ref. 18); (●) PBSIP B2; (▲) PBSIP D1.



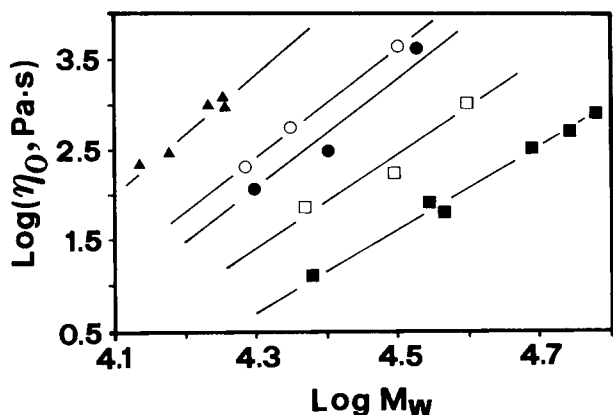
**Figure 2** Melt viscosity vs. shear rate at 200°C for PBIP and PBSIP samples with about the same  $M_w$  but with different % content of sulfonate groups as indicated on each curve: (■) PBIP L4 (from Ref. 18).

the log-log plot of vs.  $M_w$  also increases (from 5 to about 6) with ionic group content, indicating that the exponent of  $M_w$  in eq. (7) is apparently not a “universal” constant.

With increasing ionic group content, the glass transition temperature  $T_g$  also increases, as reported for some samples in Table I. In principle, the increase of viscosity, at constant molecular weight, could be due to the variation of  $T_g$ , as indicated by the well-known WLF equation. However,  $T_g$  changes only from 23 to 32°C when the ionic content increases from zero to about 15 mol %, and according to the WLF equation (applied making use of the “universal” constants), the resulting increase of the viscosity measured at 200°C would be only of the order of 20%, whereas the actual measured increase



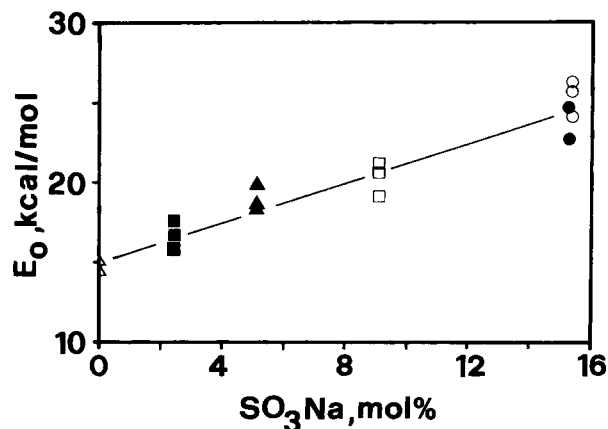
**Figure 3** “Master curve” for PBSIP samples at 200°C: (□) A1, A2, A3; (■) B1, B2, B3; (●) C'1, C'2, C'3; (▲) D1, D2, D3; (○) D'1, D'2; (—) PBIP.



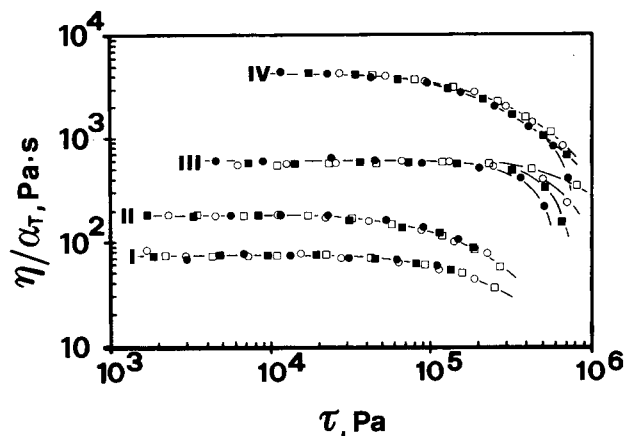
**Figure 4** Dependence of Newtonian viscosity at 200°C on the weight-average molecular weight for (■) PBIP (from Ref. 18); (□) PBSIP A; (●) PBSIP B; (○) PBSIP C'; (▲) PBSIP D, D'.

of  $\eta_0$  is of about 500 times for the 15% ionomer. The viscosity increase has therefore to be related to the presence of strong intermolecular interactions, due to the introduction of bulky  $\text{SO}_3\text{Na}$  groups, and only in a small proportion to the small increase of  $T_g$ .

The temperature dependence of viscosity is usually given by the WLF equation in the range from  $T_g$  to  $T_g + 100^\circ\text{C}$ , and by the Arrhenius-type equation above  $T_g + 100^\circ\text{C}$ . In the present work, it has been found that the activation energy for melt flow  $E_0$  of PBSIP copolymers, relative to the Newtonian viscosity,  $\eta_0$ , as obtained by using the Arrhenius equation, is higher than that of PBIP previously determined<sup>18</sup> and is also a function of ionic group content, as indicated in Table I. As can be seen in Figure 5,  $E_0$  increases linearly with increasing ionic



**Figure 5** Dependence of activation energy of Newtonian viscosity on  $\text{SO}_3\text{Na}$  content for ( $\Delta$ ) PBIP (data from Ref. 18) and PBSIP samples: (■) A; (▲) B; (□) C'; (○) D; (●) D'.



**Figure 6** "Master curves" for some PBSIP samples: (I) A2, (II) B1, (III) D'2, (IV) C'3. (□)  $T = 190^\circ\text{C}$ ; (○)  $T = 200^\circ\text{C}$ ; (■)  $T = 210^\circ\text{C}$ ; (●)  $T = 220^\circ\text{C}$ . Reference temperature  $T_0 = 200^\circ\text{C}$  for samples A2 and D'2;  $T_0 = 210^\circ\text{C}$  for samples B1 and C'3.

group concentration, and this result can indicate an increase of the size of the flow units in the Newtonian flow region. Similar behavior has been reported elsewhere in the case of poly(ethylene terephthalate) containing small amounts of sodium sulfonate groups.<sup>14</sup>

Applying the Arrhenius-type equation to viscosity data at different temperatures for a fixed value of shear stress, the activation energy at constant shear stress ( $E_\tau$ ) can be calculated. For nonionomeric polymers, one finds that  $E_\tau$  generally does not depend on  $\tau$  and is equal to  $E_0$ . This means that for a polymer sample the curves  $\eta - \tau$  at different temperatures can be superimposed by means of vertical shifts and, therefore, the time-temperature superposition principle holds.

In the case of PBSIP copolymers, the superposition was not found to be possible, especially for samples with a high content of sulfonate groups (5% or more) and high molecular weight. In Figure 6, some of the "pseudo-master curves" obtained are reported; the particular shapes of  $\eta - \tau$  flow curves, less Newtonian with increasing temperature, suggest that an increase of temperature reduces the stability of ionic aggregates, which at high temperatures can be more easily separated by the action of an external force.

## CONCLUSIONS

The introduction of  $\text{SO}_3\text{Na}$  groups in poly(1,4-butylene isophthalate) causes significant changes in the rheological behavior of the melt; in particular,

the Newtonian viscosity is largely increased and its dependence on molecular weight becomes stronger. The activation energy for melt flow is also enhanced by the presence of ionic groups and, furthermore, it was found that for poly(butylene isophthalate-co-butylene sulfoisophthalate) copolymers, with a molar content of ionic groups of 5% or higher, the time-temperature superposition principle does not hold, for samples with sufficiently high molecular weight.

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