Ion-containing polymers: 1. Synthesis and properties of poly(1,4-butylene isophthalate) containing sodium sulfonate groups

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Poly(1,4-butylene isophthalate)s containing sodium sulfonate groups were prepared from dimethyl isophthalate, 3,5-bis(carbomethoxycarbonyl) benzenesulfonate (5SIPNa) and 1,4-butanediol. Polymers of fairly high molecular weight were obtained with a content of ionic comonomeric units up to 16.7 mol%; however, increasing amounts of 5SIPNa led to a decrease in the molecular weight and to an increase in the COOH/OH terminal-group ratio. The ionomer samples were characterized for chemical structure, terminal groups, the concentration of sulfonate groups, solubility and their thermal properties. Results from different methods of terminal-group and sulfonate-group analysis were compared. Solubility was found to be strongly affected by the introduction of sulfonate groups, and samples containing 16.7 mol% of SO_3Na groups were water dispersible. D.s.c. studies on samples containing sulfonate groups, either in the free acid or sodium salt form, suggested that the effects on glass transition temperature and crystallization were due to the introduction of bulky sulfonate groups into the polymer backbone rather than to ionic interactions. Thermogravimetry showed that SO_3H groups decreased the thermal stability significantly, while SO_3Na groups had only a limited effect with respect to pure poly(1,4-butylene isophthalate).

(Keywords: ionomers; sulfonated polyesters; poly(butylene isophthalate); thermal transitions; thermal stability)

INTRODUCTION

Ion-containing polymers having a non-polar backbone and a relatively small number of ionic groups incorporated into the main chain or present as pendant groups, usually called ionomers, show very interesting properties deriving from interactions of ionic groups with the surrounding medium. The tendency of ions to aggregate in media of low dielectric constant may lead to the formation of small or large aggregates which can act as thermolabile crosslinks or as a separate phase. As a consequence of their chemical structure (chain polarity and flexibility) and of ion–ion or ion–dipole interactions, several properties of the bulk and of polymer solutions are affected. Mechanical, thermal and rheological properties are usually strongly modified, and miscibility of ion-containing polymers with otherwise immiscible polymers can also be enhanced with respect to that observed for similar polymers without ionic groups. Solubility and solution behaviour are also strongly influenced by ionic interactions, depending on ionic-group content, type of counterion and specific solvation. Several review articles and monographs have recently been devoted to this subject[1–6].

Ionomers are frequently obtained by introducing carboxyl or sulfonate groups into polymer chains by suitable reactions or by using appropriate comonomers during polymerization. The introduction of sulfonate groups by sulfonation has been proved to be an effective method for preparing ionomers with properties very different from those of the parent polymers; it has been performed successfully on several polymers including aliphatic polymers such as polystyrene[7–9], EPDM elastomers[10], and polypentenamers[11], as well as on polymers having aromatic groups in the backbone chain such as polysulfones[12–15] and poly(ether ether ketone)s (PEEK)s[16,17].

Sulfonation is especially suitable for aromatic polymers with electron-donating substituents, whereas severe reaction conditions and/or powerful sulfonating agents are needed when electron-withdrawing groups are present, as in the case of aromatic/aliphatic polyesters from aromatic diacids. However, in this case, sodium sulfonate groups can be introduced into the polyester chains by copolymerization, using the commercially available sodium 3,5-bis(carbomethoxycarbonyl) benzenesulfonate (5SIPNa) as a comonomer[18–28].

Whereas the effect of ionic groups in ionomers with a flexible aliphatic backbone has been widely studied, only few studies have been devoted to ionomers with more rigid backbones[12–17,23–28]. Recently, a few papers have

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dealt with the effects of ionic groups on some polyester properties[18–28]; the main interest was with ion-containing poly(ethylene terephthalate) (PET)[23,24,26], poly(butylene terephthalate)[27] and water-soluble polyesters[20–22,25,28]. From these papers it is clear that the properties of polyester ionomers can be changed over a broad range by changing sulfonation level and the chemical composition of the backbone polymer; it derives that many aspects of the effect of the relatively low amount of ionic groups in semiflexible polyester chains have still to be elucidated.

In this paper we report the results of the synthesis and of molecular and thermal characterization of copolyesters prepared from dimethyl isophthalate and 1,4-butanediol using various amounts of 5SIPNa as a comonomer.

EXPERIMENTAL

Products

Dimethyl isophthalate (DMIP), sodium 3,5-bis(carbomethoxycarbonyl) benzenesulfonate (5SIPNa), 1,4-butanediol (BD), $Ti(OBu)_4$, succinic anhydride, *p*-toluenesulfonic acid and potassium hydroxide were reagent grade products (Aldrich) and were used as supplied. Solvents were suitably dried and distilled before use.

Benzoic acid (Merck, volumetric standard) was sublimed under vacuum before use. Pyridine (Carlo Erba) was kept over 4 Å molecular sieves in order to trap moisture. 1,1,2,2-Tetrachloroethane (TCE) (Fluka) was shaken with concentrated sulfuric acid to remove yellowish impurities, washed with water to neutrality, dried on calcium dichloride overnight and distilled over P_2O_5 just before use.

4-Hydroxybutyl benzoate (HBB) was prepared by us, from benzoyl chloride and BD, and distilled under reduced pressure prior to use.

Polymerization

Samples were synthesized from DMIP, 5SIPNa (2–17 mol% with respect to DMIP + 5SIPNa) and BD, using $Ti(OBu)_4$ as the catalyst. The syntheses were carried out in a 1.8 l stainless steel reactor according to the usual two-stage procedure. In the first stage, at atmospheric pressure, the temperature was raised from 140 to 200°C and maintained there until more than 90% of the theoretical amount of methanol was distilled off. In the second stage the pressure was reduced to about 30 Pa while the temperature was raised to 210°C and maintained until the end of polymerization. Samples were taken from the bottom of the reactor at various times. Data relative to reaction conditions are reported in *Table 1*.

Terminal-group analysis

Carboxyl groups. Carboxyl group content was determined by direct titration of polymer solutions in chloroform using a 0.05 N methanol solution of potassium hydroxide and phenol red as the indicator. Blank runs were performed for correction. Before characterization, samples were dissolved in chloroform, washed with water to remove unreacted 5SIPNa, reprecipitated with acetone and dried at 80°C under vacuum overnight. The exact concentration of the potassium hydroxide solution was determined daily by titration with a benzoic acid solution of known concentration.

Table 1 Data relative to reaction conditions, sulfonate and terminal-group analysis

Sample	Reaction conditions (second stage), time at 210°C (min)	Ionic-group content (mol%)			Terminal-group concentration (meq kg^{-1})			
		1[a]	2[b]	3[c]	–COOH[d]	–OH[e]	–OH[f]	M_n[g] × 10^{-3}
A1	100	1.96	2.4	2.2	10.8	141.7	159.4	11.8
A2	140	1.96	2.4	–	14.2	107.0	113.0	15.7
A3	220	1.96	2.4	2.1	31.5	63.9	68.9	19.9
B1	60	4.77	5.1	5.2	17.0	151.4	182.4	10.0
B2	90	4.77	5.1	5.3	18.7	133.4	139.5	12.6
B3	180	4.77	5.1	5.9	48.5	54.7	69.7	16.9
C1	145	9.09	9.2	11.5	134.3	51.0	81.2	9.3
C2	210	9.09	9.2	10.8	142.5	12.1	42.8	10.8
C′1	54	9.09	9.1	9.3	40.4	162.3	165.5	9.7
C′2	84	9.09	9.1	10.3	47.8	127.4	130.0	11.2
C′3	144	9.09	9.1	9.8	76.1	52.4	50.4	15.8
D1	105	16.66	15.4	20.3	188.1	65.1	74.8	7.6
D2	170	16.66	15.4	20.3	197.5	23.1	33.0	8.7
D3	195	16.66	15.4	22.9	191.2	24.8	28.2	9.1
D′1	113	16.66	15.3	19.2	141.4	117.8	145.2	7.0
D′2	188	16.66	15.3	20.8	165.7	25.8	53.0	9.1

[a] Calculated from the initial molar ratio of reactants according to the equation 100 × [mol 5SIPNa/(mol 5SIPNa + mol DMIP)]

[b] Calculated from sulfur analysis (Schoeniger method) according to equation (1)

[c] Calculated from titration of $-SO_3H$ groups after ion exchange over strongly acidic cation-exchange resin

[d] Calculated from titration of –COOH groups

[e] Hydroxyl terminal groups from titration

[f] Hydroxyl terminal groups from i.r. measurements

[g] Calculated from i.r. terminal-group analysis

Hydroxyl groups: acylation procedure. Polymer samples (~ 1 g), dried overnight under vacuum at 90°C, were reacted with 0.3 g of succinic anhydride in 40 ml of nitrobenzene and 1 ml of pyridine at 150°C. Preliminary trials with increasing reaction times showed that the carboxyl group concentration attained a virtually constant value after 5 h. Reaction mixtures were cooled to room temperature and then poured, dropwise, into 400 ml of acetone. Precipitated polymers were collected by filtration and dried under vacuum at 90°C overnight. Samples of 0.6–0.8 g, weighed exactly, were dissolved in 25 ml of chloroform. Three or four 5 ml portions from each solution were in turn titrated with a 0.05 N potassium hydroxide solution in methanol, using phenol red as the indicator. Blank runs were performed for correction. The hydroxyl concentration was calculated by subtracting the carboxyl concentration obtained as described above.

Hydroxyl groups: infra-red spectrophotometric method. I.r. spectra of samples dissolved in TCE were recorded on a Bruker model IF48 *FT*i.r. spectrophotometer using a Beckman variable-path NaCl cell with a path length of 0.2 cm. A calibration plot of absorbance *versus* hydroxyl group concentration in the range 1×10^{-3}–1×10^{-2} mol l^{-1} was constructed with HBB solutions in TCE. The absorbance of the band centred at 3617 cm^{-1} was measured by the peak height method. Absorptivity calculated from the calibration plot was equal to 139.9 l mol^{-1} cm^{-1}. Polymer samples were thoroughly dried under vacuum at 90°C overnight before preparing the solutions for spectroscopic investigation to eliminate moisture that gives rise to two strong peaks centred at 3600 and 3675 cm^{-1} respectively, which interfere with the free hydroxyl group peak at 3617 cm^{-1}. The results from terminal group determination are reported in *Table 1*.

Sulfonate-group analysis

Four different methods were used to determine sulfonate groups. Elemental analysis and flame photometry were performed on a Carlo Erba 1120 elemental analyser and a AA30 Varian atomic absorption spectrophotometer, respectively.

An oxygen flask combustion procedure, according to the Schoeniger method, was also performed; the combustion products were titrated with a N/100 solution of $Ba(ClO_4)_2$ in alcohol medium. The sulfur weight per cent (S%) obtained in this way was used to calculate the ionic-group content according to the equation:

$$\begin{aligned}\text{ionic-group content (mol\%)} &= 100\ (\text{S\%}/32.06)/\{(\text{S\%}/32.06) \\ &\quad + [100 - 322.26\ (\text{S\%}/32.06)/220.23]\} \\ &= 100\ [220.23\ \text{S\%}/(3206 - 102.03\ \text{S\%})]\end{aligned} \tag{1}$$

Finally, an ion-exchange treatment was performed on samples dissolved in chloroform/methanol (5/1, v/v) using a glass column filled with Amberlist 15 (Aldrich) acidic cation exchange resin suspended in chloroform/methanol (5/1). The acidic samples were recovered by precipitation with cyclohexane. This elution procedure did not significantly alter the molecular weight (intrinsic viscosity) of the initial samples. The same procedure already described for carboxyl group titration was applied to acidic samples to determine the total amount of sulfonic plus carboxylic groups. Sulfonic-group concentration was determined by subtracting the carboxyl group content from the total amount of acidic groups.

Solubility tests

Solubility was checked at low and high temperature in various solvents at 1% w/v concentration. When present, the insoluble fraction was filtered and weighed; results are reported in *Table 2*.

Table 2 Solubility data

		Sample[a]																	
		A3		A3 (acidic form)		B3		B3 (acidic form)		C3		C3 (acidic form)		D′2		D′2 (acidic form)		PBIP	
Solvent	Dielectric constant	c	h	c	h	c	h	c	h	c	h	c	h	c	h	c	h	c	h
Acetone	20.7	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I
$CHCl_2COOH$	8.2	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
$CHCl_3$	4.9	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
CH_3OH	32.6	I	I	I	I	I	I	I	I	I	PS	I	I	I	PS	I	I	I	I
$C_6H_5NO_2$	34.8	I	(S)	I	(S)	I	(S)	I	(S)	I	S	I	PS	I	S	I	PS	I	(S)
m-Cresol	11.8	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Dioxane	2.2	I	(S)	I	(S)	I	(S)	I	(S)	I	PS	I	(S)	Sw	PS	I	(S)	I	(S)
DMF	36.7	I	(S)	I	(S)	I	(S)	I	(S)	I	(S)	I	(S)	I	S*	I	(S)	I	(S)
DMSO[b]	46.7	I	I	I	I	I	(S)	I	(S)	I	(S)	I	(S)	I	S*	I	S*	I	(S)
Pyridine	12.3	I	Sw	I	Sw	I	Sw	I	Sw	I	Sw	I	Sw	PS	S	I	S	I	Sw
THF	7.6	I	(S)	I	(S)	I	(S)	I	(S)	I	Sw	I	PS	I	Sw	I	PS	I	Sw
Toluene	2.4	I	I	I	I	I	I	I	Sw	I	Sw	I	Sw	I	Sw	I	I	I	(S)
Water	78.5	–	–	–	–	I	I	–	–	I	PS	I	I	I	S*	I	I	I	I

[a] Solubility tests were performed on 1% w/v solutions, at room (c) and high (h) temperatures. I, Completely insoluble; S, completely soluble (samples remain soluble at room temperature when solubilized at high temperature); (S), soluble at high temperature, reprecipitate after several hours or some days; S*, opalescent solution; PS, partially soluble; Sw, swelling

[b] These data are referred to dry DMSO, also small percentages of moisture make samples C3 and D′2 soluble

Thermal characterization

Glass transition, melting and crystallization were studied using a Perkin-Elmer Series 7 d.s.c. instrument. To obtain transition temperatures, samples were heated up to 180°C in a first run, cooled at $10°C\,min^{-1}$ and reheated at $10°C\,min^{-1}$. The glass transition temperature, T_g, was taken as the mid-point of the transition in the second heating run, and the melting temperature, T_m, as the maximum of the highest endothermic peak. The change in heat capacity (ΔC_p) at T_g and the corresponding width of the temperature range (ΔT_g) in which it occurs were also derived from these curves. Samples were also submitted to annealing treatments before d.s.c. experiments: typically, they were heated for 30 min at 165°C, quenched to room temperature, annealed at 71°C for 16 h and scanned at $10°C\,min^{-1}$.

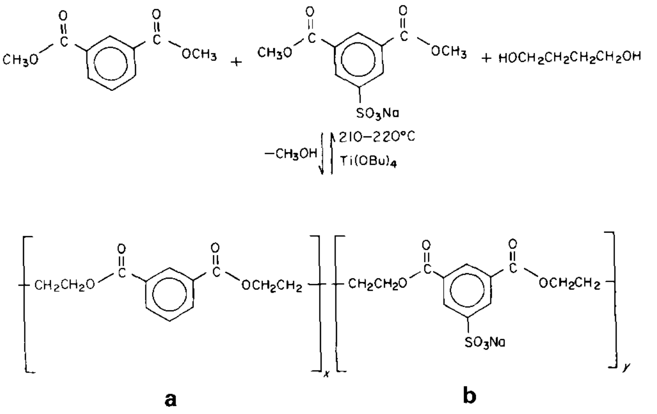
Weight loss curves were obtained using a Perkin-Elmer Series 7 TG instrument with a heating rate of $20°C\,min^{-1}$ in air and under nitrogen.

RESULTS AND DISCUSSION

Synthesis

Copolyesters containing various amounts of ionic groups were prepared by the usual two-stage melt polycondensation from DMIP, 5SIPNa and BD using $Ti(OBu)_4$ as the catalyst, according to the reaction in *Scheme 1.*

In comparison with the synthesis of the corresponding homopolyester, poly(1,4-butylene isophthalate) (PBIP)[29], few major differences were observed in the presence of sulfonate groups: (i) an increase in the COOH/OH end-group mole ratio; (ii) a reduction of the maximum molecular weight attainable; and (iii) a more abundant production of tetrahydrofuran (THF) from side reactions. These effects increased when the initial amount of 5SIPNa increased. Similar effects to those of points (i) and (ii) can be found in the literature for other types of polyesters[21,22,24]; however, other literature data[30,31] seem to exclude a direct effect of sulfonate groups on reaction kinetics. Instead, these effects can be reasonably explained assuming that they derive from side reactions involving hydrolysis of ester groups. Hydrolysis can occur in a more extensive way in the presence of ionic groups due to the higher amount of moisture retained (either adventitious or formed during polymerization from direct esterification). As an effect of hydrolysis there is the formation of a higher amount of acidic groups, which in turn can explain the increasing amount of THF and the reduction of the maximum molecular weight attainable. In fact, it is known that acidic groups catalyse the dehydration of BD, with the formation of THF plus water[32,33] and, when the relative amount of carboxyl groups becomes high, there is a stoichiometric imbalance between carboxyl and hydroxyl terminal groups, an inhibiting effect of acidic groups on $Ti(OBu)_4$ catalyst[34], and an ever-increasing rate of chain cleavage by hydrolysis. All these effects can account for the observed decrease in the maximum molecular weight attainable. Accordingly, attempts to prepare a polymer from BD and 5SIPNa were absolutely unsuccessful due to the complete transformation of the iniital BD into THF. Nevertheless, copolymers with fairly high molecular weights were obtained for initial amounts of 5SIPNa as high as 16.7 mol%.



Scheme 1

Due to interchange redistribution reactions, easily occurring in the presence of $Ti(OBu)_4$ under our experimental conditions, sulfoisophthalic moieties are expected to be randomly distributed along the chains. Both i.r. and ^1H n.m.r. spectra were consistent with the chemical structure expected.

Terminal-group analysis

Terminal-group analysis is frequently used to derive information on the relative amount of carboxyl and hydroxyl terminal groups in polyesters. The quantitative analysis of these terminal groups is a useful method for the evaluation of the number-average molecular weight when all terminal groups are carboxyl or hydroxyl, and their number per chain is known (two for linear chains, more for branched ones).

In the present case, this method is particularly important for the molecular weight characterization, since other alternative methods (osmometry, light scattering, g.p.c., etc.) can lead to misleading results due to strong intermolecular ionic interactions.

Under our reaction conditions, polymer chains were expected to be linear and the terminal groups to be hydroxyl and carboxyl groups. Although the possibility of the presence of small numbers of other types of terminal groups could not be ruled out, they were not detected by spectroscopic methods. With this reservation in mind, the number-average molecular weight, M_n, was calculated from –COOH and –OH group content, assuming two functional groups for each chain and neglecting cyclic molecules.

Several methods have been described in the literature for the quantitative evaluation of these groups[35,36], the most frequently used being titration and i.r. measurements.

Carboxyl end-group concentration can be easily and accurately measured by titration. Titration can also be used to measure hydroxyl end-group concentration; in this case hydroxyl groups must be completely transformed by a suitable reaction before titration. We used a method proposed for poly(1,4-butylene terephthalate)[37] which employs a nitrobenzene solution of succinic anhydride to transform –OH groups into –COOH groups. The method for hydroxyl group titration takes a longer time and is sometimes less precise than for carboxylic groups, as it requires that the original polymer is dissolved, reacted and recovered by precipitation before titration. It is possible that a fraction

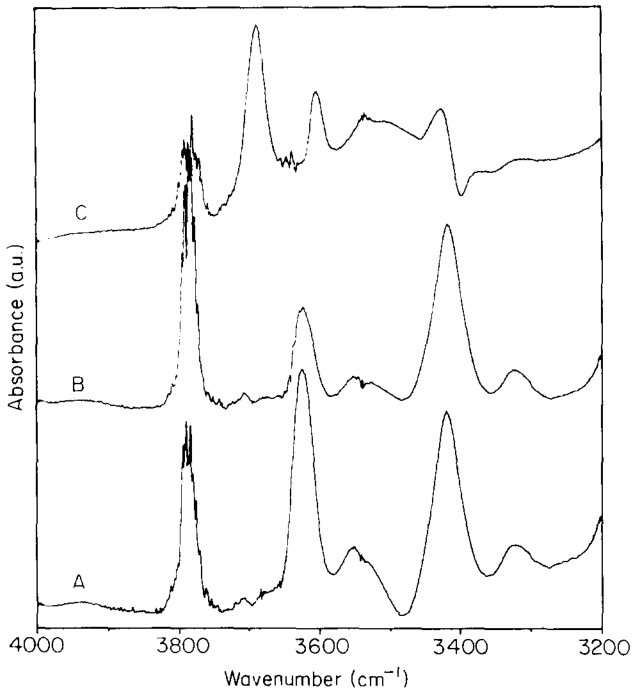


Figure 1 *FT*i.r. spectra of the OH stretching region for: A, a sample of PBIP homopolymer; B, sample D3, dried; C, sample D3, wet

of low molecular weight oligomers is lost during this treatment.

I.r. measurement of the –OH stretching band has been proposed in the literature for the analysis of hydroxyl groups in polymers[35,36,38,39]. This method is more rapid than titration once a calibration curve is constructed; however, it can suffer from poor accuracy either when the –OH concentration becomes quite low (for example, for high molecular weights) or when other bands interfere. The ability of hydroxyl groups to form hydrogen bonds, both between themselves and with other functional groups, can lead to a difficult interpretation of spectra because of a number of factors which can influence the equilibrium concentration of associated groups. Despite this, i.r. spectroscopy has been successfully used for the quantitative determination of hydroxyl groups in polymers[39], provided that a suitable calibration has been performed.

In the present paper, 4-hydroxybutyl benzoate was used, alone or in mixtures with *p*-toluenesulfonic acid (PTSA) and/or sodium *p*-toluenesulfonate, to calibrate the i.r. method. No interference was observed in the presence of PTSA, but the presence of ionic groups makes the system more hydrophilic and accurate drying is required to avoid interference from the bands of water (see *Figure 1*).

Results of COOH and OH concentrations from both titration and i.r. measurements are reported in *Table 1*. As mentioned above, the COOH/OH ratio increases with the 5SIPNa content, due to side reactions.

The hydroxyl concentration measured by titration was always slightly lower than that obtained by the i.r. method. The main reason can be ascribed to the small amount of linear oligomers which is lost during the manipulation of samples, because a small fraction of oligomers can remain soluble after reprecipitation in the procedure used to transform hydroxyl into carboxyl groups for titration. In contrast, using the i.r. method all the OH groups are measured. In fact, when i.r. measurements were performed on samples submitted to the same procedure of dissolution and reprecipitation used to transform hydroxyl into carboxyl groups, the hydroxyl concentration was in good agreement with that measured by titration.

Analysis for sodium-sulfonate groups

The content of SO_3Na groups in the final polymer can differ from the nominal content because a fraction of monomers can remain unreacted at the end of polymerization, or can be preferentially removed as a volatile product from the reacting system together with BD during the second stage of polymerization. For this reason samples were analysed for the SO_3Na group content. Several methods of analysis have been compared recently[40], namely, a combustion–spectrophotometric method for sulfur, flame photometry for counterion, titration of SO_3H groups after ion-exchange treatment on an acidic cation exchange resin, and a dye-sorption method. Except for the last, the results from the various methods have been claimed to be in sufficiently good agreement when applied to PET containing SO_3Na groups.

We also tested several methods: sulfur elemental analysis performed by an elemental analyser suffered from poor precision and accuracy, and considerably higher values were obtained from the flame photometry method when Na^+ was the counterion, probably as a consequence of adventitious Na^+ contamination during sample manipulation. Titration with an alcohol solution of KOH was performed on samples after ion-exchange treatment on an acidic cation exchange resin. By this method, the overall amount of acidic groups was derived, from which the number of SO_3H groups was obtained by subtracting the initial amount of COOH groups. Every sample was eluted in duplicate, and two or more titrations were performed for each eluted sample. Whereas very good precision was found for different titrations of the same eluted sample, poor precision was observed for samples eluted at different times, particularly for samples with a high ionic-group content. When the initial amount of 5SIPNa increased, the titration method gave average results increasingly higher than the values expected from the initial amount of reactants (see *Table 1*). Results in closer agreement with the initial amount of 5SIPNa were obtained from the oxygen flask combustion technique according to Schoeniger (see *Table 1*).

From both titration and oxygen flask combustion methods it appears that the content of ionic groups in the polymer is similar to that expected from the feed, and does not change significantly with polymerization time.

Solubility behaviour

The solubility of a polymer in a solvent is a function of the specific interactions between constitutional units of the polymer and molecules of the solvent, and can be fairly well predicted from the knowledge of the relative solubility parameters. When ionomers are considered, the main contributions to the free energy of mixing, and therefore to solubility, may become ion–ion and ion–dipole interactions, which depend in a complex manner on the polar nature and flexibility of the polymer backbone, on the nature of counterion, and on the solvation capability of the solvent. Therefore, in the case of ionomers, solubility is usually not predictable.

Qualitatively, it is known that ionic associations which characterize ionomers make the dissolution of these materials difficult in solvents of low polarity, and solubility decreases when the concentration of ionic groups increases. In polar solvents, or in the presence of a small amount of a polar cosolvent, capable of solvating ionic species, the solubility behaviour can change dramatically and in some cases, depending upon the backbone chemical structure, the presence of ionic groups can make ionomers soluble in water[20,22,25,28].

We have examined the solution behaviour of sulfonated PBIP in a variety of different solvent systems; specifically, the effects of solvent type and sulfonation level have been examined. The typical behaviour of sulfonate-containing ionomers is coupled with the intrinsic limited solubility of PBIP and therefore most of our samples were soluble in a very limited number of solvents; the solubility characteristics of the various sulfonated PBIP samples both in the salt (Na^+ counterion) and in the free acid form are presented in *Table 2*.

Among the more common low-boiling solvents, PBIP itself was only fully soluble at room temperature in chlorinated solvents or in solvents with a relatively high capacity to form hydrogen bonds. The introduction of 5SIPNa units was expected to modify strongly the solubility and, indeed, samples with a high sulfonation level were soluble in a few solvents which can be considered relatively polar, as defined by a high dielectric constant, where the unsulfonated PBIP is completely insoluble. In particular, it is interesting to note that sample D′2, containing 16.7 mol% of sulfonate units, gave a slightly opalescent solution even in water. Samples with lower degrees of sulfonation show an intermediate solubility or behave like unsulfonated PBIP. Little difference was observed in the solubility behaviour of the same sample in the salt or acidic form. The presence of sulfonate groups either in the Na salt or acidic form permits dissolution of these polymers even at rather high concentration of alcohols or other polar cosolvents, where unsulfonated PBIP would not be soluble.

THERMAL TRANSITION BEHAVIOUR

Influence of sulfonation level on the glass transition

The influence of sulfonate groups, either in the free acid or in the sodium salt form, on the glass transition was studied by d.s.c. experiments; the relative data are reported in *Table 3*.

For samples with a low content of SO_3Na groups ($\leqslant 5$ mol%) the T_g values, recorded at 10°C min^{-1} heating rate after cooling from the melt at 10°C min^{-1}, were similar to those observed for pure PBIP under the same conditions. T_g increased for samples with higher sulfonation levels; however, throughout the concentration range studied, the increase is lower than that previously observed for ionomers with different polymer backbone, such as sulfonated polystyrene[9], Nafion[41], EPDM[42], polypentenamer[11] and PEEK[16,17]. On the other hand, the increase in T_g is higher than that reported for Na-sulfonated PET[24], although in this case T_g was probably a complex result of opposite effects deriving from the simultaneously increasing amount of sulfonate groups and diethylene glycol moieties. Furthermore, different results are reported from different authors in the case of poly(aryl ether sulfone)[12–15]. From these results it is evident that the influence of ionic groups on T_g is largely dependent on the ionomeric structure, that is on the nature of the polymer backbone, the statistical distribution of the sulfonic groups along the chain, and the type of counterion. A further result deriving from the observation of the d.s.c. curves of our samples, was that there was no evidence of a second phase, as would be expected in the case where a large fraction of the ions existed in the form of large ionic domain. When samples with sulfonate groups in the free acid form were run under the same conditions, a linear increase in T_g (from 23.1 to 37.7°C) was obtained as the level of sulfonate groups increased from 0 to 16.7 mol%; in this case the T_g values of samples in the free acid form were 2–5°C higher than those of the corresponding Na sulfonate samples. This result appears quite different from that previously reported for sulfonated poly(ether sulfone)[11] and for acrylic acid/ethyl acrylate-based ionomers[12].

It has been frequently assumed that the main reason for the increase in T_g of ionomers derives from ionic interactions leading to ion-clustering or physical crosslinks; however, in the present case, our data suggest that the main contribution to the enhancement of T_g derives from the introduction of bulky sulfonate groups (either in the free acid or sodium salt form) and from hydrogen bond interaction. In other words, for samples with SO_3Na groups the contribution from ionic

Table 3 Data of thermal characterization

	Thermal treatment[a]					
	1		2			
Sample	T_g (°C)	ΔC_p ($J\,g^{-1}\,°C^{-1}$)	T_g (°C)	ΔC_p ($J\,g^{-1}\,°C^{-1}$)	T_m (°C)	ΔH_m ($J\,g^{-1}$)[b]
PBIP	23.1	0.25	27.6	0.14	141.6	35.0
A1	22.8	0.29	26.8	0.10	141.8	38.8
A1(acid)	25.2	0.29	27.2	0.17	135.2	30.5
B1	23.7	0.32	24.3	0.28	137.3	12.5
B1(acid)	27.3	0.32	26.9	0.34	124.6	1.2
C′1	25.9	0.30	26.0	0.34	128.1	0.6
C′1(acid)	31.0	0.36	31.8	0.34	–	–
D′2	32.0	0.24	34.5	0.24	–	–
D′2(acid)	37.7	0.32	31–39	0.25	–	–

[a] 1, 10°C min^{-1} heating rate, after cooling at 10°C min^{-1} from 180°C; 2, 10°C min^{-1} heating rate, after annealing at 71°C for 16 h

[b] Including the enthalpy of the small endothermic peak 30–40°C lower than the main peak

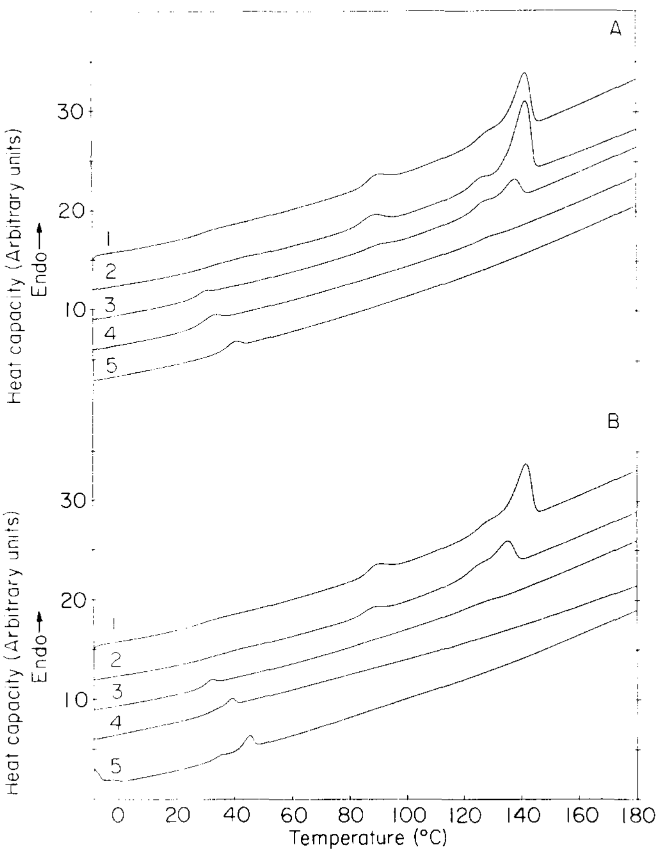


Figure 2 D.s.c. curves of sulfonated PBIP samples: (A) sulfonate groups in the sodium salt form; (B) sulfonate groups in the free acid form. 1, PBIP; 2, sample A1; 3, sample B1; 4, sample C'1; 5, sample D'2

aggregation seems to be negligible, and the increase of T_g appears more likely to be the result of internal chain stiffening due to the presence of sulfonate groups. Unfortunately, a lack of knowledge of the T_g for the fully sulfonated PBIP does not permit us to verify whether the increase in T_g obeys the simple random copolymer equation[43]. In any case, from our results it appears that ion-clustering effects can be ruled out for our samples, as suggested by other authors for different ionomers[15,43].

Effects of ion interaction should also be reflected in the broadening of the temperature range where the glass transition occurs (ΔT_g), and in a decrease of the increment of heat capacity at T_g (ΔC_p)[8,11,17,24]. The broadening of ΔT_g is a well known phenomenon which has been ascribed to the presence of structural fluctuations with ion-poor and ion-rich domains, which lead to a spectrum of local T_gs, as in the immediate vicinity of ionic domains the chains are constrained in conformation of higher free energy. Neither for the acid, nor for the sodium salt form of our samples, did we observe a significant broadening of ΔT_g.

Also, the effect of sulfonated moieties on ΔC_p at T_g appeared quite unusual for our samples; in fact, we observed an increase with sulfonation level (except for sample D'3 with 16.7 mol% of SO_3Na groups) while a decrease was found for sulfonated PEEK[17], ascribed to the presence of physical crosslinking. It is again interesting to note that the presence of SO_3H groups has a slightly stronger effect on ΔC_p than the presence of SO_3Na groups. Such evidence is further proof that for the sodium salts of sulfonated PBIP the clustering effects due to ion aggregation should be negligible, if they exist.

D.s.c. experiments were also performed on samples annealed at 71°C for 16 h after quenching from the melt; under such conditions crystallization occurs for some samples (see below) and the influence of sulfonation level on T_g, ΔT_g and ΔC_p is the result of contributions deriving from the bulky sulfonate groups, interchain interactions, and degree of crystallinity. From the data reported in *Table 3*, the changes with sulfonation level appear complex. At low sulfonation level it seems that crystallization has a much stronger effect than ionic or hydrogen bond interactions; however, for the amorphous sample D'2 with a high content of SO_3Na, a small increase in T_g was observed with respect to the unannealed one. Annealing also led to changes in the shape of the d.s.c. curve around T_g for sample D'2 in the acidic form, where there is evidence of multiple transitions (see *Figure 2*). Similar effects were found for sulfonated polystyrene[8] and ascribed to an excess enthalpy associated with ageing.

Crystallinity

PBIP has an intrinsically low crystallization rate, and did not crystallize at all when cooled from the melt at 10°C min^{-1}. However, it crystallized (degree of crystallization was about 18% from the enthalpy of fusion of 100% crystalline sample previously calculated[44]) when annealed at 71°C for 16 h (see *Table 3* and *Figure 2*).

The introduction of bulky sulfonate groups into the chains (either in the acid or in the sodium salt form) is expected to further reduce the degree of crystallization[27]. Indeed, we did not observe any trace of melting in the d.s.c. curves of samples cooled from the melt at 10°C min^{-1} and the enthalpy of fusion was found to decrease when the concentration of sulfonate groups was increased (either in the acid or sodium salt form) for samples annealed at 71°C. In this latter case, any trace of melting endotherm disappeared completely when the sulfonation level was higher than 9 mol%. Parallel to the decrease of the main melting peak, we observed the decrease of a small endothermic peak, 30–40°C lower than the main melting transition, which was observed previously for other polyisophthalates[44]. Similarly, samples B1, C'1 and D'2 did not show any trace of melting after annealing at 90°C for 1 h, while pure PBIP and sample A1 showed a small melting peak.

Two main effects can be assumed to prevent crystallization of sulfonated samples: a copolymer effect due to the introduction of bulky sulfonated units in the polymer chains, and the promotion of physical crosslinking due to interactions between ions or hydrogen bonds. Again, as observed for glass transition, the SO_3H groups seem to be more effective in preventing crystallization than SO_3Na groups, suggesting that the effect due to ion interactions is very limited, if it exists.

It is noteworthy that sample A1, which contains a low level of ionic groups, behaves quite differently from samples B1, C'1 and D'2, showing a slightly higher temperature and enthalpy of melting than pure PBIP both when annealed at 90°C for 1 h and at 71°C for 16 h. In this case, the small content of ionic groups seems to favour crystallization instead of preventing it. Under the same conditions, sample A, with sulfonate groups in the free acid form, crystallized but showed a lower T_m and enthalpy of melting.

Thermal stability

Thermogravimetric analysis (t.g.a.) has been performed under air and nitrogen on both the sodium salt and free acid forms of our samples; typical curves (relative to

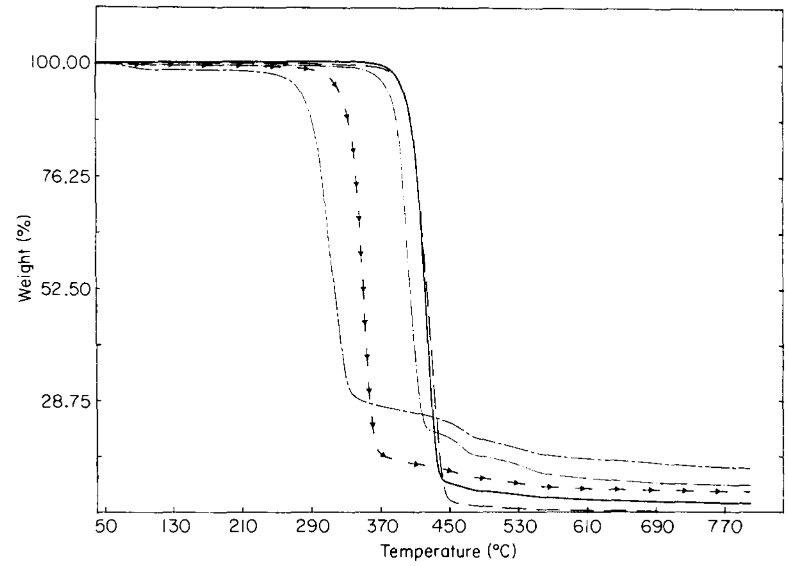


Figure 3 Thermogravimetric curves: ——, pure PBIP; →→, sample B3 in the free acid form; ——, sample B3 in the sodium salt form; – - –, sample D'2 in the free acid form; —·—, sample D'2 in the sodium salt form

samples B3 and D3) recorded under nitrogen are shown in *Figure 3* together with that of unsulfonated PBIP; similar results were obtained when t.g.a. curves were recorded in air.

Figure 3 shows that there are very limited effects due to the presence of sodium sulfonate groups; there is a limited shifting towards lower temperatures of the maximum rate of weight loss, and the solid residue at temperatures higher than 450°C increases with increasing SO_3Na group content. These results are quite similar to those reported for PET containing SO_3K groups[26].

On the other hand, the effect due to the presence of SO_3H groups is much more pronounced (the shift towards lower temperatures is about 80–110°C) and increases when the sulfonation level T.g.a. curves are usually the result of very complex phenomena involving chemical reactions, diffusion and volatilization of molecular fragments deriving from decomposition of the polymer, and can be considered as indicative of the thermal stability of the polymer. Therefore from our results we can infer that the thermal stability of samples with sulfonate groups in the sodium salt form is higher than the thermal stability of samples containing free acid groups, a conclusion which is in agreement with results previously reported for sulfonated PEEK[16,17], although we did not observe a change in the shape of the weight loss curves as found for sulfonated PEEK[16].

In previous papers, desulfonation reactions have been invoked to explain changes in t.g.a. curves for sulfonated PEEKs with high thermal stability[16,17]. However, for our samples the complex degradation pathway discussed in ref. 15 seems more appropriate. In fact, as the shifting of the curves at lower temperatures is accompanied by a weight loss which is much higher than expected from the sulfonation level, we must conclude that it cannot be ascribed completely to the decomposition of sulfonic groups.

For the samples considered in this work, other degradation reactions, probably acid-catalysed reactions induced by the presence of SO_3H groups, gave a more significant contribution to the weight loss. Thermal degradation reactions producing non-volatile pyrolysis compounds such as inorganic sulfates or sulfites, suggested by other authors[45], can explain the higher residue at high temperatures; however, they cannot be detected by t.g.a. curves only, and should be confirmed by appropriate alternative methods.

CONCLUSIONS

Polyesters containing sulfonate groups were prepared from DMIP, BD and 5SIPNa by the usual two-stage crystallization. The increasing amount of comonomer containing ionic groups in the reaction mixture led to samples with a higher COOH/OH end-group ratio and to a decrease of the final molecular weight. Nevertheless, copolymers of fairly high molecular weight were obtained even for initial amounts of 5SIPNa as high as 16.7 mol%. Parent samples, with the sulfonate groups in the free acid form, were obtained by eluting the original ones on an ion exchange resin.

The solubility characteristics of the various samples were those usually found for ionomers: the higher the sulfonation level, the higher the solubility in polar solvents. Samples containing about 16.7 mol% of ionic groups also became dispersible in water.

The presence of SO_3Na ionic groups does not have a significant effect on the thermal stability with respect to unsulfonated PBIP. On the contrary, the thermal stability is strongly reduced for the samples containing SO_3H groups. The increase of T_g with sulfonation level was lower than usually found for different ionomers, and T_g values were slightly higher for samples having the sulfonate groups in the acidic form. Therefore we concluded that the main contribution to changes in T_g derives from the introduction of bulky sulfonate groups rather than from ion interactions. A comparison of our data with evidence reported in the literature about the effect of ionic interactions on T_g, leads to the conclusion that the chemical structure of the backbone polymer plays a fundamental role in the capability for the system to originate a physical crosslinking or ion clustering. The presence of sulfonate groups also influences the crystallization behaviour, and again when sulfonate groups are in the acidic form the effects are slightly stronger than for the sodium salt form.

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REFERENCES

1 Lundberg, R. D. in 'Encyclopedia of Polymer Science and Engineering' (Ed. J. I. Kroschwitz) Interscience, New York, 1987, Vol. 8, p. 393

2 Pineri, M. and Eisemberg, A. (Eds) 'Structure and Properties of Ionomers', Reidel, Dordrecht, 1987

3 Tant, M. R. and Wilkes, G. L. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* 1988, **C28** (1), 1

4 Fitzgerald, J. J. and Weiss, R. A. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* 1988, **C28** (1), 99

5 Mauritz, K. A. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* 1988, **C28** (1), 65

6 Lantman, C. W., McKnight, W. J. and Lundberg, R. D. in 'Comprehensive Polymer Science' (Eds C. Booth and C. Price) Pergamon, Oxford, 1989, Vol. 2, p. 755

7 Makowski, H. S., Lundberg, R. D. and Singhal, G. H. US Patent 3 870 841, 1975 (to Esso Res. and Eng. Co.); *Chem. Abstr.* 1974, **81**, 153695

8 Weiss, R. A. *J. Polym. Sci. Polym. Phys. Edn* 1982, **20**, 65

9 Weiss, R. A., Lundberg, R. D. and Turner, S. R. *J. Polym. Sci. Polym. Chem. Edn* 1985, **23**, 549

10 Makowski, H. S., Lundberg, R. D., Westerman, L. and Bock, J. *Am. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* 1978, **19** (2), 292

11 Rahrig, D., McKnight, W. J. and Lenz, R. W. *Macromolecules* 1979, **12**, 195

12 Noshay, A. and Robeson, L. M. *J. Appl. Polym. Sci.* 1976, **20**, 1885

13 Sivashinsky, N. and Tanny, G. B. *J. Appl. Polym. Sci.* 1983, **28**, 3235

14 Johnson, B. C., Yilgor, I., Tran, C., Iqbal, M., Wightman, J. P., Lloyd, D. R. and McGrath, J. E. *J. Polym. Sci., Polym. Chem. Edn* 1984, **22**, 721

15 Drzewinski, M. and MacKnight, W. J. *J. Appl. Polym. Sci.* 1985, **30**, 4753

16 Xiao Jin, Bishop, M. T., Ellis, T. S. and Karasz, F. E. *Br. Polym. J.* 1985, **17**, 4

17 Bailly, C., Williams, D. J., Karasz, F. E. and MacKnight, W. J. *Polymer* 1987, **28**, 1009

18 Kibler, C. J., Lappin, G. R., Shields, S. J., Hawkins, J. M. and Wooten, W. C. Jr US Patent 3 546 008, 1970 and US Patent 3 779 993, 1973 (to Eastman Kodak Co.); *Chem. Abstr.* 1969, **71**, 82289

19 Fritz, J., Roux, P. and Neel, J. US Patent 4 048 149, 1977 (to Rhone-Progil); *Chem. Abstr.* 1974, **81**, 92214

20 Williams, R. C. in 'Encyclopedia of Polymer Science and Engineering' (Ed. J. I. Kroschwitz), Interscience, New York, 1987, Vol. 12, p. 310

21 Zhang Hog, Li Shengping and Luo Honglie, *J. Appl. Polym. Sci.* 1987, **34**, 1353

22 Chen, K. M. and Liu, H. J. *J. Appl. Polym. Sci.* 1987, **34**, 1879

23 Ostrowska-Czubenko, J. and Ostrowska-Gumkowska, B. *Eur. Polym. J.* 1988, **24**, 65

24 Ostrowska-Gumkowska, B. and Ostrowska-Czubenko, J. *Eur. Polym. J.* 1988, **24**, 803

25 McCartney, T. L. and Piirma, I. *Polym. Bull.* 1990, **23**, 367

26 Ostrowska-Gumkowska, B. and Ostrowska-Czubenko, J. *Eur. Polym. J.* 1991, **27**, 681

27 Gorda, K. R. and Peiffer, D. G. *J. Polym. Sci. Part B. Polym. Phys.* 1992, **30**, 281

28 Kotera, N., Taki, H., Takaki, M. and Takahashi, K. *Polym. Bull.* 1992, **27**, 673

29 Pilati, F., Munari, A., Manaresi, P., Milani, G. and Bonora, V. *Eur. Polym. J.* 1987, **23**, 265

30 Vejrosta, J., Zelena, E. and Malek, J. *Coll. Czech. Chem. Commun.* 1978, **43**, 424

31 Grobe, H., Nissen, D. and Rossbach, V. *Makromol. Chem.* 1975, **176**, 2839

32 Hudson, B. G. and Backer, R. *J. Org. Chem.* 1967, **32**, 3650

33 Buyle Padias, A. and Hall, H. K. Jr *J. Polym. Sci., Polym. Chem. Edn* 1981, **19**, 1021

34 Pilati, F., Manaresi, P., Fortunato, B., Munari, A. and Passalacqua, V. *Polymer* 1981, **22**, 799

35 Boiko, V. P. and Grishchenko, V. K. *Acta Polym.* 1985, **36**, 459

36 Siggia, S., Hanna, J. G. and Stengle, T. R. in 'The Chemistry of the Hydroxyl Group' (Ed. S. Patai), Interscience, New York, 1971, Vol. 1, Ch. 6

37 Borman, W. F. H. *J. Appl. Polym. Sci.* 1978, **22**, 2119

38 Kim, C. S. Y., Dodge, A. L., Lan, S. F. and Kawasaki, A. *Anal. Chem.* 1982, **54**, 232

39 Tompa, A. S. *Anal. Chem.* 1972, **44**, 628

40 Ostrowska, J., Ostrowska-Gumkowska, B., Rybinska, D. and Szymansky, G. *Acta Polym.* 1985, **36**, 691

41 Yeo, S. C. and Eisemberg, A. *J. Appl. Polym. Sci.* 1977, **21**, 875

42 Agarwal, P. K., Makowski, H. S. and Lundberg, R. D. *Macromolecules* 1980, **13**, 1679

43 Otocka, R. E. P. *J. Macromol. Sci. Chem.* 1971, **5**, 275

44 Yip, H. K. and Williams, H. L. *J. Appl. Polym. Sci.* 1976, **20**, 1209

45 Bothe, N., Döscher, F., Klein, J. and Widdecke, H. *Polymer* 1979, **20** (2), 850