POLY(ETHER-BLOCK-SULFONATED ESTER) COPOLYMERS. III. MORPHOLOGY AND IONIC AGGREGATION IN PESE

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ABSTRACT

Sulfonated poly(ether–ester) copolymers (PESE) based on poly(butylene terephthalate-*co*-butylene 5'-sulfoisophthalate sodium salt) and poly(1,4-oxytetramethylene) were studied. Morphological changes that can occur as a consequence of interactions of the sulfonate groups in PESE were investigated by using differential scattering calorimetry (DSC), wide- and small-angle x-ray scattering, and scanning electron microscope measurements. The x-ray scattering and DSC studies show that the degree of crystallinity decreases with increasing content of ionic groups in the polyester rigid segments. This change is the result of ionic forces caused by incorporation of the ionic units. A morphology of ionic aggregates inside microphase-separated poly(butylene terephthalate) domains is suggested.

Key Words: Sulfonated poly(ether–ester); Sulfonated polyester; Ionomers; Polyester elastomers; Morphology; Microphase separation

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INTRODUCTION

Extensive research has been devoted to understand the structure–property relationships of ionomers, polymers containing a small fraction of ionic units (1–3). It is generally known that mechanical properties, morphology, and viscosity are strongly influenced by the aggregation of ionic groups into ionic microdomains, forming physical crosslinks, as a result of ionic interactions (3,4). Correlations between the undeformed morphology of the ionomers and their physical properties have proved vital to understand the role of ionic aggregation in determining the unique properties of this type of materials. Many studies have been made on the structure of ionic aggregations (multiplets or clusters) and the structure–property relations (2,4,5). Several structural models for the ionic aggregates have been proposed, such as a core-shell structure (6), a lamellar structure or a cylindrical structure (7), a ball-like structure of pseudocrystalline array (8), and a hard sphere model (4,5).

The study of block ionomers (3,4,9), such as ionic unit-modified polyurethanes (10,11), shows that the molecular interactions which are responsible for the stability of the domain structure can be increased by incorporation of ionic groups in the rigid segments; this results in improvement of the phase separation and strength of the materials. Similar results were observed for triblock copolymers, such as sulfonated styrene-*b*-hydrogenated butadiene-*b*-sulfonated styrene (SEBS) (12), where it was established that sulfonated polystyrene segments (SPSs) aggregate into spheres suspended in the hydrogenated butadiene matrix. Within the SPS phase, the sulfonated groups phase separate into ionic-rich domains. In the light of the above results, it was thought interesting to check the joint effect of the ionic interactions and crosslinking in a poly(ether-*b*-ester) system.

In particular, the poly(ether-ester) (PEE) has been subject to many modifications by a variety of units (13–15) and its use as thermoplastic elastomers is well known (16). So far, the influence of incorporation of ionic units in the PEE system has not been studied. The interest in these systems follows from the attempt to combine the possibility of ionic aggregation (clustering) of classical ionomers with the formation of crystalline domains by the rigid segments in the flexible polyether matrix.

This paper represents a part of our ongoing study of the effect of intermolecular interactions on the morphology and properties of sulfonated poly(ether-*block*-ester)s (PESEs) containing ionic units in the rigid polyester segments. Recently, in our previous papers (17,18), we reported the phase structure and physical properties of PESEs. Investigations of the mechanical and dielectric relaxations of these PESEs show the presence of specific phenomena, which may be connected with the occurrence of ionic aggregates (multiplets or clusters). By using wide- and small-angle x-ray scattering (WAXS, SAXS) methods, more detailed information about the influence of the concentration of ionic units in rigid polyester segments of PEE on the morphology can be obtained.

EXPERIMENTAL

Materials

A series of poly(ether-*block*-sulfonated ester) copolymers (PESE) consisting of 30 and 50 wt% of poly(butylene terephthalate-*co*-butylene 5'-sulfoisophthalate sodium salt) (SPBT) segments and poly(1,4-oxytetramethylene) (PTMO) flexible segments was used. As illustrated in formula (1), the PESE consists of the flexible segment of PTMO ($\bar{M}_n = 1000$ g/mol, Terathane 1000, Du Pont, USA) and the rigid segment of random sequences of poly(butylene terephthalate) (PBT) and poly(butylene 5-sulfo-isophthalate).

Samples containing: 0, 2.5, 5, 7.5, 10 mol% of the sodium salt of 5-sulfoisophthalate comonomer units in the 50 wt% rigid segment copolymer, and samples containing: 0, 5, 7.5, 10, 15, 20 mol% of the sodium salt of 5-sulfoisophthalate comonomer units in the 30 wt% rigid segment copolymer were used. In addition, in order to determine the influence of the ionic groups on the semicrystalline rigid segments, the PBT and its sulfonated analog, SPBT, containing 5 and 10 mol% of ionic units were also investigated.

(1)

The composition and sample designation are given in Table 1. The samples of PESE and sulfonated PBT were prepared by melt polycondensation as described in our previous report (17). Samples for x-ray diffraction investigations were prepared by compression molding at about 3.5 MPa at a temperature approximately 10°C higher than the melting point determined by differential scattering calorimetry (DSC) (Table 1).

Measurements

Wide-angle x-ray scattering: WAXS experiments were carried out by using a Rigaku-Denki SG-9 Geigerflex diffractometer (Japan). Diffraction patterns were recorded in the 2θ -range from 5 to 35° with a step of 0.05° at room temperature. Ni-filtered Cu K α radiation with a wavelength of 1.5418 Å (30 kV, 20 mA) was used. Determination of the crystalline phase content in the polymers was calculated by using the method of Hindeleh and Johnson (19,20). According to this

Table 1. PESE and Modified PBT Samples Used in Study

Sample	x_h (wt%)	Content of SBI in Rigid Segment (mol%)	T_m DSC (°C)	w_c DSC (%)
30/0	30	0	162	16.2
30/5	30	5	152	14.4
30/7.5	30	7.5	148	12.7
30/10	30	10	147	12.4
30/15	30	15	138	11.5
30/20	30	20	131	7.2
50/0	50	0	194	24.9
50/2.5	50	2.5	190	23.6
50/5	50	5	186	22.1
50/7.5	50	7.5	182	20.2
50/10	50	10	182	19.8
PBT	100	0	215	44.1
SPBT-5	100	5	211	41.1
SPBT-10	100	10	210	38.5

x_h : rigid segments content; T_m , w_c : melting point and degree of crystallinity determined by DSC.

method, each measured profile was decomposed into the individual crystalline peaks and an amorphous halo whose decomposition was achieved by a least-squares fit of the measured profile with the theoretically calculated curve. In attaining the least-squares fit, we assumed each fundamental profile to be a linear combination of Gaussian and Cauchy functions. A third-order polynomial was used for the background scattering profile. The peak positions, peak heights, peak widths, relative abundance of Gaussian and Cauchy functions, and parameters of the polynomial were used as variables. The degree of crystallinity was calculated as the ratio of the total area under the resolved crystalline peaks to the total area under the x-ray scattering curve.

Small-angle x-ray scattering: SAXS patterns were obtained with a Kratky compact camera (SWAXS, Anton Paar KG, Austria). Measurements were performed in the θ -range from 0.11 to 5° with a step of 0.011°. Analysis of the SAXS curves was based on the standard theory for pseudo-two-phase lamellar systems. Values of the long period L of each sample were determined from the position of the first maximum of the correlation function $\gamma(r)$ (21–23). The number-average values of the thickness l_c of the crystalline layers and the thickness E of the transition layer between crystalline and amorphous regions were calculated by similar methods as described for anionically modified poly(ethylene terephthalate) (24).

Scanning electron microscope measurements: The morphology of the PESE samples were examined by using a JSM-6100 SEM (JEOL, Japan). The cryogenically fractured surfaces of the injection-molded specimens were coated with thin film of gold before SEM observation.

RESULTS AND DISCUSSION

Three series of wide-angle x-ray diffraction (WAXD) patterns for PESE and SPBT taken at room temperature are shown in Figs. 1–7. The dotted line is the experimental curve, whereas the continuous line presents the separation into crystalline peaks and amorphous halo. The PESE copolymers show a well-defined set of crystalline diffraction peaks. The observed peaks have been assigned to crystal planes as presented in Table 2 for sulfonated PBT, PESE 50/0 and PESE

Figure 1. WAXD patterns of the copolymers containing 30 wt% of rigid segments modified by 0 and 5 mol% of SBI units.

Figure 2. WAXD patterns of the copolymers containing 30 wt% of rigid segments modified by 7.5 and 10 mol% of SBI units.

50/10 in comparison with those for nonsulfonated PBT. As the content of ionic units in the polyester segment increases in the series, the PBT crystalline peaks remain in the same positions. For SPBT, a marked reduction in the relative scattering intensity is observed with increasing sulfonation units, with an absence of well-defined scattering peaks in the 10 mol% sample (Fig. 7). While eight peaks

Figure 3. WAXD patterns of the copolymers containing 30 wt% of rigid segments modified by 15 and 20 mol% of SBI units.

can be assigned in the spectrum of nonmodified PBT and PEE (13,25) (Table 2), the spectrum of the 10 mol% sample shows a broad halo. In the spectrum corresponding to SPBT-10 sample, the peak (010) is grossly reduced in intensity, and the peaks: (1 $\bar{1}$ 1), (01 $\bar{1}$) have disappeared. In addition, all our diffraction

Figure 4. WAXD patterns of the copolymers containing 50 wt% of rigid segments modified by 0 and 2.5 mol% of SBI units.

patterns of PESE contain a prominent component at about $2\theta \approx 20^\circ$; a very broad peak is required here for good fit to be obtained. This peak is attributed to the amorphous (halo) part of the material. The crystalline PTMO gives the main reflection at $2\theta \approx 20.2^\circ$, but PTMO crystallizes in PEE only when $\bar{M}_n$ is higher than 1000 g/mol (26).

Figure 5. WAXD patterns of the copolymers containing 50 wt% of rigid segments modified by 5 and 7.5 mol% of SBI units.

The crystal lattice of PBT has been reported by many investigators (26–32); two triclinic crystalline configurations were found, i.e., an α -form and a β -form (27–29). Normally, the α -form is stable in the relaxed state (27,30), and the β -form occurs under stretching (31), comprising more extended chains than in the α -form. The transition between the two forms that takes place is reversible by

Figure 6. WAXD patterns of the copolymer containing 50 wt% of rigid segments modified by 10 mol% of SBI units.

mechanical deformation: from the α -form to the β -form by elongation to about 12% or more, and inversely by relaxation (31,32). The difference in periods of the two crystalline forms is due to the conformational change of the four-methylene sequences and the adjoining C—O bond in both forms (27,29). The β -form has a larger period of identity and shows a greater density than the stable form. The intense (11 $\bar{1}$) reflections in the α -form are much weaker than the β -form. Cooper et al. (26) have found that the individual crystallites in PEE are 20–40 Å thick in the chain $\langle 001 \rangle$, $2\theta \approx 8.8^\circ$ direction of the crystal and 60–110 Å in the transverse directions $\langle 010 \rangle$ and $\langle 100 \rangle$. Unfortunately, the (001) reflections in the data collected so far have been too weak to allow any sensible estimation of lamellar thickness from this reflection. Indeed, this reflection disappeared completely in the sulfonated copolymers. In Table 3, the main WAXD reflections of SPBT and PESE containing 5 and 10 mol% of ionic units in rigid segments are compared to those from α - and β -form PBT (27–29). The comparison of d -spacings was limited to the interplanar spacings: $d(100)$, the distance between parallel packed layers of terephthaloyl residues; $d(010)$, the interplanar distance in the direction of ester bonding, and $d(0\bar{1}1)$ (28). As shown in Tables 2 and 3, and Figs. 1–7, it appears that the sulfonated copolymers have about the same main d -spacings as semicrystalline PBT (27–29). Thus, PESE and SPBT may be crystallized in the α -form of PBT. The crystalline form of the undrawn SPBT sample (see Fig. 7) could not be identified because of the broad WAXD, but it may be the α -form under no stress (31). It is natural from the above observations that the lamellar crystals of the α -form grow from the melt and the solution (26,31).

Figure 7. WAXD patterns of sulfonated PBT, containing 5 and 10 mol% of SBI units.

In Table 4, the SAXS data are presented, as well as the calculated WAXS degree of crystallinity (ϕ_c) for the PESE and SPBT copolymers. For the PESE copolymers, a very small reduction in degree of crystallinity was observed, but in the case of SPBT, the changes in crystallinity were greater. For SPBT, a large reduction in the relative scattering intensity with increasing ionic unit

Table 2. Peak Positions (as Equivalent Bragg Spacings d) for PBT, SPBT, PESE 50

Peak Number	Angle 2θ (°)	d -Spacing (Å)	Relative Intensity	Plane
PBT				
1	8.78	10.07	4	(001)
2	15.85	5.59	8	(011)
3	17.25	5.14	23	(010)
4	20.70	4.29	14	($\bar{1}$ 11)
5	23.26	3.82	100	(100)
6	25.29	3.52	33	(1 $\bar{1}$ 1)
7	29.32	3.04	10	(101)
8	31.05	2.88	9	($\bar{1}$ $\bar{1}$ 1)
SPBT-5				
1	15.67	5.65	43	(0 $\bar{1}$ 1)
2	17.24	5.14	52	(010)
3	20.69	4.29	64	($\bar{1}$ 11)
4	23.25	3.82	100	(100)
5	30.15	2.96	27	(1 $\bar{2}$ 0)
SPBT-10				
1	23.4	3.80	100	(100)
PESE 50/0				
1	8.87	9.97	16	(001)
2	15.87	5.58	74	(0 $\bar{1}$ 1)
3	17.20	5.15	97	(010)
4	20.46	4.34	100	($\bar{1}$ 11)
5	23.25	3.82	98	(100)
6	24.83	3.58	70	(1 $\bar{1}$ 1)
7	29.14	3.06	26	(101)
8	31.10	2.88	26	($\bar{1}$ $\bar{1}$ 1)
PESE 50/10				
1	15.9	5.58	65	(0 $\bar{1}$ 1)
2	17.31	5.12	88	(010)
3	20.69	4.29	100	($\bar{1}$ 11)
4	23.25	3.82	95	(100)
5	24.83	3.58	89	(1 $\bar{1}$ 1)
6	29.25	3.04	30	(101)
7	30.74	2.91	29	($\bar{1}$ $\bar{1}$ 1)

content was observed. The disappearance of well-defined scattering peaks in the sample containing 10 mol% of ionic units (sample SPBT-10, Fig. 7) suggests that the sample has a very small degree of crystallinity (10%). However, the absence of sharp crystalline reflections in SPBT does not indicate a total absence of crystallinity (33). The asymmetry of the PBT profile indicates the presence of some crystallinity.

Poly(butylene terephthalate) containing different levels of sulfonated units was also studied by Gorda and Peiffer (3,25). They investigated the morphology of

Table 3. Main Wide-Angle X-Ray Reflections of PBT, SPBT and PESE

Sample	(100)		(010)		(011)		Reference
	d^o (Å)	d^c (Å)	d^o (Å)	d^c (Å)	d^o (Å)	d^c (Å)	
PBT (α -form)	3.79	4.00	5.13	5.27	5.46	5.64	Nietzsche (27,28)
PBT (β -form)	3.71	3.53	5.19	5.18	5.55	5.88	Yokouchi (28)
PBT (α -form)	3.838	3.842	5.124	5.122	5.513	5.514	Liu and Geil (29)
SPBT-5	3.82		5.14		5.65		— ^a
PESE 30/0	3.84		5.15		5.72		— ^a
PESE 30/5	3.85		5.12		5.70		— ^a
PESE 30/10	3.85		5.14		5.71		— ^a
PESE 50/0	3.82		5.15		5.58		— ^a
PESE 50/5	3.84		5.15		5.64		— ^a
PESE 50/10	3.82		5.12		5.58		— ^a

d^o : observed d -spacing for PBT by Yokouchi et al. (27,28); d^c : calculated d -spacing for PBT by Nietzsche et al. using molecular simulations (27,29).

^a Present study.

SPBT by WAXS, polarized light microscopy, and small angle light scattering. It was found that the SPBT shows markedly lower crystallinity, less than 30%, in the samples with higher levels of sulfonation and the type of spherulitic structure in these polyesters depends upon the sulfonation level, as does the degree of crystallinity. At the lower ion contents (≤ 4.9 mol%), the SPBT have the so-called unusual spherulitic morphology. The morphology of SPBT copolymers changes

Table 4. WAXS Scattering and SAXS Data

Sample	Content of SBI (mol%) ^a	ϕ_c (%)	L (Å)	$\langle l_c \rangle$ (Å)	E (Å)
30/0	0	17.6	110	30.2	48.7
30/5	5	16.6	138	31.8	32.8
30/7.5	7.5	16.0	116	26.4	43.0
30/10	10	15.6	232	31.4	21.1
30/15	15	12.2	—	—	24.0
30/20	20	12.0	200	34.0	16.3
50/0	0	23.7	100	28.0	30.0
50/2.5	2.5	22.0	214	35.0	32.3
50/5	5	23.2	222	35.6	28.1
50/7.5	7.5	20.0	188	39.2	28.6
50/10	10	21.3	202	35.6	32.3
PBT	0	—	—	—	—
SPBT-5	5	26.7	—	—	—
SPBT-10	10	10.6	—	—	—

ϕ_c : degree of crystallinity calculated from WAXS; L : long period; $\langle l_c \rangle$: thickness of crystalline layers; E : thickness of the transition between crystalline and amorphous regions.

^a In rigid segments.

from abnormal to normal spherulitic superstructure in the range of 5–8.4 mol% sulfonated content and complete disappearance of the spherulitic morphology was observed at higher sulfonate contents (13.5 mol%).

SAXS was used for two purposes: (i) to obtain characteristic values for the microstructure, i.e., the long period (L); (ii) to obtain information about the ionic peak which is present at low angles and is characteristic for ion containing materials; the ionic peak corresponds to interparticle (8) or intraparticle (4) interference from ionic aggregates. The appearance of the latter peak in SAXS patterns is generally accepted as evidence of ionic aggregation. The SAXS curves for the PESE samples are shown in Figs. 8 and 9. For all of these PESE samples a diffraction maximum on the SAXS curves was observed. It seems most likely that the maximum on the SAXS curves is connected with the presence of a lamellar structure of the hard polyester domains rather than with the existence of ionic aggregates. However, it cannot be completely excluded that the observed maximum is a result of an overlap of both effects. Thus, the influence of ion aggregation on the morphology of PESE can be explained only indirectly based on the difference in the behavior of the copolymers and PBT homopolymer.

The decrease of maximum intensity for PESE containing 30 wt% of polyester segments can be connected with the decrease of degree of crystallinity which is confirmed by the WAXS and DSC (18) (see w_c and ϕ_c in Tables 1 and 3) measurements. However, PESE containing 50 wt% of polyester segments shows higher values of the maximum intensity than the PEE that is not modified by ionic units (Fig. 9). If the degree of crystallinity for these copolymers does not increase, then the increase in peak intensity can be explained by the existence of ionic

Figure 8. SAXS curves of PESE containing 30 wt% of polyester segments modified by ionic units.

Figure 9. SAXS curves of PESE containing 50 wt% of polyester segments modified by ionic units.

aggregates, whose occurrence is masked by the high degree of crystallinity. The decrease in intensity in the case of PESE containing 30 wt% of polyester segments could be explained by the small content of segments which are able to crystallize, which are, in turn, additionally disturbed by ionic groups which, as a result of the association of ionic groups, destroy the local order. Aggregation of ionic groups seems to be in competition with crystallization and, as a result, polymers modified by ionic groups are characterized by lower crystallinity. Some authors (4) suggested that ionic aggregation takes place much more rapidly than does crystallization and it proceeded more fully only after the ionomer aggregates have developed. The other explanation for reduction of the degree of crystallinity and melting temperature is a change in length of the rigid blocks. When the fraction of PTMO sequences is kept constant in the copolymers, the introduction of sulfonated meta-linked phenylene units into the rigid segments can decrease the PBT segment block length, because the isophthalate units are shorter but have larger volume due to the SO_3Na group than terephthalate units.

On the basis of the WAXS results, i.e., the lack of significant changes in unit cell spacings and increasing or decreasing in peak breadth, we can conclude that the ionic units (SBI) introduced into the rigid segments do not co-crystallize with the terephthalate units. It can also be supposed that replacing a portion of the terephthalic acid (BT) in the rigid segments with a second acid, such as sodium salt of 5-sulfoisophthalic acid (thus an increasing SBI content), would lead to the formation of an ionic bonding system and hence to a gradual decrease in melting temperature as shown by the DSC data (17,18). Usually, the principal effect of strong ionic interaction is a strong influence on the flow

characteristics of a polymer system as long as the thermal energy of the system is below what is necessary to promote thermal dissociation of the ionic aggregations (3). Hence, in semicrystalline materials incorporating ionic bonding, one finds increases in the melt viscosities and in relaxation times, but reductions in the rate of crystallization and melting temperature. A different behavior was observed in the case of sulfonated polystyrene block copolymers (12,34). For these copolymers, as might be expected, a significant increase of the softening point over that for the unsulfonated polymer was observed as an effect of the association of the ionic groups. The rubbery plateau was also greatly enhanced. Tsujita's group (35,36), which examined the crystallization of ethylene ionomers in detail, suggested that in crystalline ionomers two types of crystallites are present: chain-folded lamellae and bundlelike crystals which melt at higher and lower temperatures, respectively. The lower melting temperature shifts to higher temperatures with increasing annealing time, even in the presence of ionic aggregates, confirming that the presence of ionic aggregates does not immobilize the chain. Such mobility of chains was confirmed by the work of Gomez et al. (3,37) on syndiotactic styrene ionomers, which suggests that the kinetics of crystallization in that system can be used as a measure of the internal viscosity or of chain mobility in ionomers.

A two-phase morphology of the PESE system composed of a pure SPBT crystalline phase and an amorphous phase, which is a homogenous mixture of PTMO segments and uncrystallized SPBT sequences (18), has been proposed. Depending on the rigid segment content, a more or less continuous crystalline super-structure is formed of single crystal lamellae tied together by short sequences of rigid segments. The faces of the lamellae are tied to each other through the amorphous regions, which are combinations of flexible PTMO and uncrystallized PBT tie linkages.

The use of the correlation function calculated from the SAXS curve enables a more accurate characterization of the lamellar structure in PESE copolymers; the data are presented in Table 4. Changes in the structural parameters would be expected due to the strong intermolecular interactions between ionic groups. The average thickness of the crystalline layers (l_c) for PESE containing 50 wt% of polyester segments (50/0-10 series) is higher than for the nonionic copolymer. The thickness of the transition regions (E) for PESE containing 30 wt% of polyester segments decreases (excluding sample 30/7.5) with increasing ionic groups content, but for PESE containing 50 wt% of polyester samples, it seems to be independent of the ionic content in the polyester segments. We have not found any explanation why the 30/7.5 sample differs. The decrease may be the effect of a sharpening of the phase boundary between crystalline and amorphous regions as a result of increasing polarity of the crystalline phase connected with the presence of ionic groups in this phase. The long period (L) is a measure of the average distance between crystallites and, as such, is the sum of the average thickness of the crystalline layers and the amorphous regions. All samples exhibit an increase of long period L with increasing ionic units in the polyester segments. This suggests

that the increase is in the amorphous phase rather than in the crystalline phase. The increasing value of long period may also be connected with stretching (stressing) of the polymer chains caused by ionic aggregation. The increase in stressing is a result of ionic intermolecular interactions and depends on the distance between ionic groups (units) in the polymer backbone, and the length and stiffness of the backbone segments in the immediate vicinity of these ionic groups, which are held by ionic pairs in the multiplets. Stressed sequences of rigid segments close to the multiplet move more slowly and cannot be part of folded-chain lamellae. They become, with the ionic aggregates, part of the amorphous region with uncrystallized PBT linkages.

The influence of orientation on the structure of PEE containing PBT segments has been studied by Fakirov et al. (38,39) using SAXS. These investigations show that in the strained state the initial long spacing L_0 increases linearly with the deformation up to a value of $\varepsilon = 80\%$ (L_1) and then steeply decreases down to a value $L_2 \approx L_0$, i.e., very close to its initial value L_0 . Semicrystalline PBT consists of microfibrils being connected by a large number of tie molecules. In this way, the amorphous phase can be considered as intrafibrillar (the main portion) and interfibrillar. The increase in L can be explained in terms of an extension of the chains in the amorphous regions. Higher deformations cause a pulling out of tight tie molecules connecting crystals in adjacent microfibrils and relaxing some of the fibrils. On the basis of these results, we suppose that stressing of polymer chains by ionic aggregation can be compared with stressing in oriented polymers. In the case of PESE, the increasing long period is connected with stressing the polymer chain caused by ionic aggregations or with the formation of small ionic aggregates in the crystalline phase or by the change of structures built up of lamellae. In fact, the long period corresponds to the average distance between adjacent PBT crystallites, which are separated by the amorphous phase composed of PBT disordered segments (including ionic groups) and the flexible segments. Some fractions of the PBT segments may be in the amorphous phase near the crystallites as well as in the crystalline lamella; the ionic aggregates could be located in both phases.

Usually, in a crystallizable polymer backbone, ionic groups reduce the fractional crystallinity but the ionic groups do not become part of the crystal lattice, as shown in poly(ethylene-co-acrylic acids) ionomers (3,40). However, considering the results obtained in these investigations, we rather suggest that in PESE the aggregates of ionic groups reside within the crystalline domains, i.e., between lamellae in the lamellar stacks.

Scanning electron microscope photomicrographs of the fracture surfaces of PEE nonmodified by ionic units (samples 30/0, 50/0) and sulfonated PEE (samples 30/10, 50/7.5) are shown in Figs. 10 and 11. The overall morphology of the sulfonated PEEs is similar to that of the semicrystalline nonmodified PEE copolymers. However, the occurrence of separate small areas (particles, domains) is clearly visible in the samples containing ionic units in the rigid segments. We suggest that these separated particles are ion-rich hard domains.

(a)

(b)

Figure 10. SEM photomicrographs of the fracture section of PEE containing 30 wt% of rigid segments: (a) nonmodified by ionic units (sample 30/0); (b) modified by 10 mol% of ionic units (sample 30/10).

The appearance of significant differences, particularly for samples 50/0 and 50/7.5 (Fig. 11(a) and (b)), shows that the presence of ionic units in the rigid segments changes the morphology and as a result, the physical properties (18) of PESE.

(a)

(b)

Figure 11. SEM photomicrographs of the fracture section of PESE containing 50 wt% of rigid segments: (a) nonmodified by ionic units (sample 50/0); (b) modified by 7.5 mol% of ionic units (sample 50/7.5).

CONCLUSIONS

To evaluate the effect of ionic group incorporation in a series of PEEs, the copolymers were examined by SAXS and WAXS methods. Changes in all structural parameters, as can be expected, are due to the strong ionic interactions between ionic groups incorporated in the rigid polyester segments. The data obtained from this study showed that the degree of crystallinity decreased with increasing content of ionic groups in the polyester rigid segments. While ionic aggregation is the primary driving force for phase separation in these materials, their morphology more closely resembles that of nonionic PEE than that of conventional ionomers. This is because the ionic groups exist in blocks composed primarily of rigid polyester residues. A morphology of ionic aggregates inside lamellar stacks was suggested. These polar crystalline polyester hard domains are dispersed in the flexible polyether matrix. The soft phase is a homogeneous mixture (with its own T_g) of flexible PTMO segments and uncrystallized PBT sequences rejected from the crystalline phase.

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