The Glass Transition, Crystallization, and Melting Characteristics of a Class of Polyester Ionomers

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ABSTRACT: The glass transition temperature (T_g), crystallization, and melting character of a class of random polyester ionomers (polymer containing < 10 mol % ionic groups) were investigated. The nonlinear change of the T_g and crystallization and melting behavior were characterized using differential scanning colorimetry (DSC). The ionomers are derived from polyethylene terephathalate (PET) modified through copolycondensation with a fully neutralized sulfonate moiety (sodiosulfo) isophthalate (Na-SIP). Significant and systematic changes in the glass transition temperature and thermal characteristics upon addition of Na-SIP on the PET backbone were observed, indicating strong association and interaction on the ionic species. At Na-SIP levels $\geq$ 4 mol %, the turn of the the glass transition temperature was found, and the same results were obtained for the samples treated either by quenching or dissolution, sug-

gesting the presence of reversible crosslink and aggregation of the ionic species within the organic matrix. When crystallized from the healing or cooling the samples during the DSC nonisothermal crystallization run at a 10°C/min, the enthalpy of the cold crystallization and melting showed an obvious decrease with the increase of Na-SIP content, and changes of the crystal temperature had an analogy to those of the T_g. A tune of the crystal temperature was found at Na-SIP levels $\geq$ 3 mol % (see Figs. 4, 5, and 7). The experimental data were discussed in the context of the restricted mobility model of the aggregation in the ionomers. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3660–3666, 2002

Key words: ionomers; polyester; glass transition; crystallization

INTRODUCTION

Most of the studies on ionomers to date have been limited to addition-type polymers, for example, polyethylene, polystyrene, and polyisobutylene, with only a few cases in which the ionic functionalities are introduced via a condensation process. In this article we reported on the glass transition response and thermal characteristics of a class of polyester ionomers derived from polyethylene terephathalate (PET) modified at random by a fully neutralized sulfonate moiety, (sodiosulfo) isophthalate (Na-SIP) from 2 to 9 mol % contents (concentration > 9 mol % DSC curves would show multiple peaks, the crystal and melting enthalpy cannot be calculated exactly). More complete morphologic and thermal characterization of these materials is described elsewhere.[1]

Currently, ionomeric polyesters are used further in bicomponent fiber to get a variety of effects, very low denier fibers, and for fibers that finally are free from the ionic comonomer and that the concentration of ionic comonomers in the ionomeric polyester is varied in a low range because the higher content will lead to

higher melt viscosity and difficult spinning. However, the presence of a small amount of covalently bonded ionic moieties in organic polymers is known to exert a profound effect on their chemical and physical properties. Indeed, ionomers have been shown to exhibit considerably higher stiffness, higher glass transition temperature, and higher melt viscosity than their nonionic homologs. The properties change, as stated above, is generally attributed to the formation of ionic aggregates within the organic matrix, which act as thermoreversible crosslinks and effectively retard the translational mobility of the polymer chains.[2] The exact form and size of these aggregates is still open to debate, but their existence, as evidenced from small-angle X-ray scattering (SAXS), neutron scattering, and other techniques, is firmly established, at least for some materials.[3]

Although glass transition temperature and thermal characteristics are not ideally suited to probe the structure and organization of the ionic aggregates, they are very sensitive to the concentration of ionic species and number of aggregates, and can effectively complement other, are more direct, have characterization of techniques, and provide useful insights. Any factor affecting the ionic associations and their interaction with the surrounding organic matrix, for example, the structure of ionic moiety and the degree of neutralization, the flexibility of the polymer backbone, ore more-
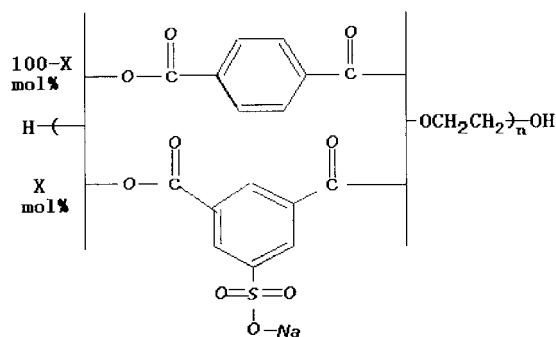
Figure 1 Molecular structure of ionomeric polyester.

over, the presence of plasticizers, should also influence the glass transition temperature and thermal properties. Indeed, these effects have been corroborated in many studies on a wide variety of ionomeric systems.[3]

EXPERIMENTAL

Materials

The materials used were: terephthalic acid (TPA; Fiber level Yangtze Corp., China) Ethylene glycol (EG; Fiber level Yangtze Corp., China), and 5-(sodiosulfo) isophthalate (20% bisglycol ester solution Huitong Corp., China).

The production of the resins was carried out in a batch condensation process using a high pure terephthalic acid route in a 20-L reactor (Fourne Bonn Universal-Polycondensation-Anlage Pu20 Universal-Polycondensation-Plant Pu20 Ger.).

All the polymers of this study are polyethylene terephthalate modified at random through copolycondensation by 5-(sodiosulfo) isophthalate (Na-SIP)—a fully neutralized sulfonate moiety (Fig. 1). These polymers are designated P-X, where X = mol % Na-SIPA of total di-acid moieties. Thus, in accordance with this convention, the unmodified polyester (PET) would be designated P-0, while a resin containing 4 mol %Na-SIP is P-4. It should be noted that the total molar concentration of Na-SIP is half the value represented by X if the polyester is viewed as an AB-type copolymer. In this study X was varied in the range from 0 to 9 mol % Na-SIP concentration (the crystal and melting peak would show multiple peaks when X > 9 mol %, result in the crystal and melting enthalpy cannot be

exactly calculated). The polyester ionomers were synthesized in two steps by step-growth polymerization in a manner similar to PET.

Transesterification

The reactor were charged with 5 kg (30 mol) TPA, 3 kg (48 mol) EG in large excess while a catalyst, 0.35 g $Co(OAc)_2$ and the inhibitor of DEG,[4] 2.5 g NaOAc were added, N_2 was led, and the reactor pressure was maintained at 0.25 Mpa/cm^2, 60 min fully stirring at 180°C. Then the reactor was heated to 250°C. Transesterification had been in progress and water had begun to reflux up the column. The reaction was continued for 100 min, and the reactor temperature was raised gradually over the next 60 min to 275°C. When the theoretical volume of water quantity out of the reactants amounted to 1200 mL or so, the reaction was stopped. The intrinsic viscosity of prepolymer was lower than 0.07dL/g, and the degree of esterification is greater than 80%.

Polycondensation

In a continuous process, 2.5 g $Sb(OAc)_3$, a polycondensation catalyst and Na-SIP (20%bis-glycol ester solution) were added with a stoichiometric amount (depending on the desired Na-SIPA concentration) to a terephthalic acid monoethylene glycol prepolymer. The mixture was fully stirred for 60 min under high vacuum (20 Pa) at 250°C; then it was polycondensed with continuous stirring at 275°C. Vacuum was at 10 Pa. An ammeter was used to measure the power needed to stir at the required rate and monitor the buildup in viscosity (molecular weight). When the reacting polymer-melt reaches the set melt-viscosity (the torque meter show the value), the vacuum is broken with N_2, and the melt is extruded into strands that are solidified, cut into small chips, crystallized at 145°C, and dried to very low moisture content. The polymerize time of the samples reaching the set melt-viscosity are listed in Table I.

Intrinsic viscosity

The intrinsic viscosity (IV) was used to characterize the molecular size of the polyester ionomers. This property was measured at 25°C with a solvent mixture

TABLE I
List of Material

Sample No.	1	2	3	4	5	6	7
[a]Poly.time(min)	160	150	122	105	85	66	45
Composition	P-0	P-2	P-3	P-4	P-6	P-7	P-9
IV (dL/g)	0.690	0.518	0.477	0.438	0.393	0.383	0.369

[a] Polymerization time was set according to the same melt-viscosity for P-0–P-9.

TABLE II
Composition and Glass Transition Temperature of the Samples

Sample	1	2	3	4	5	6	7
Composition	P-0	P-2	P-3	P-4	P-6	P-7	P-9
T_{g1} (°C)	78.9	77.8	75.5	74.4	75.7	76.1	76.6
T_{g2} (°C)	77.2	76.5	75.0	74.5	76.2	77.0	78.2

T_{g1} Glass transition temperature of the quenched samples.
T_{g2} Glass transition temperature of the samples treated with trifluoacctic acid/chloroform solution.

of phenol/acetylene tetrachloride (50/50 by wt) at a concentration of 0.22 g/dL. All the ionomeric solutions were filtrated with arenaceous glass filter. At such a low concentration, the measured IV is a close approximation of the intrinsic viscosity of the polymer, which is more directly associated with its molecular weight. It is considered a good solvent for the solvent system to dissolve the ionomeric polyester. The dissolved time shows that the dissolved speed of the ionomeric polyester is quicker than PET. Also, the solvent system of phenol/acetylene tetrachloride (50/50 by wt) is a good solvent for PET. Therefore, it is unable to show the spherical shape in the very low concentration.

The samples prepared by this procedure are listed in Table I, together with their respective intrinsic viscosities. The compositions of the samples listed in Table I represent nominal values, as determined from the reaction stoichiometry, rather than actual concentrations. However, the element analysis data (based mainly on X-ray fluorescence quantitative analysis of atomic sulfur) indicate that these values are reasonable approximations.

Quenching procedure

Because of the acute sensitivity of the polyester ionomers to heated history, all the samples in this study were thoroughly quenched prior to DSC testing. Typically, the samples were raised to 300°C under Nitrogen, held for 10 min, and the samples were rapidly put into the liquid nitrogen. Then the samples were taken to the sealed test tube for testing.

Solvent treatment

Another group of samples treated with solvent were tested to eliminating the affection of the few catalyst and other compositions that were not polymerized for the accuracy of DSC testing.

Procedure

The samples were dissolved respectively in the solution of trifluoacetic acid/chloroform (3 : 1 w/w) (7% resin concentration) with vigorous shaking to form a uniform dispersion. After the samples were fully dissolved, they were respectively coated on a glass plate then soaked rapidly in nonionic water to form a film and were fully washed using nonionic water for 20 h to neutralization (pH 7). The samples were dried in vacuum (20 Pa) at 100°C for 72 h and then transferred under a nitrogen blanket in to a vacuum desiccator for further drying prior to testing.

DSC measurement

DSC was performed to study the T_g and other thermal behavior. A Perkin-Elmer DSC-7 apparatus equipped with TAS-7 software and a Perkin-Elmer PE-7700 professional computer was utilized. Temperature calibration was performed with indium and zinc. Calibration

TABLE III
Crystallization and Melting Behavior of the Quenched Samples

Composition		Heating Run				cooling Run	
Samples	SIP (mol) %	T_{c1} (°C)	$-\Delta H_{c1}$ (J/g)	T_m (°C)	ΔH_m (J/g)	T_{c2} (°C)	$-\Delta H_{c2}$ (J/g)
1	P-0	138.1	34.39	265.4	55.74	222.7	44.30
2	P-2	136.8	29.07	258.2	50.85	223.3	37.51
3	P-3	136.4	26.23	241.4	35.22	214.0	28.66
4	P-4	142.7	26.16	240.0	27.98	216.6	26.74
5	P-6	153.8	24.09	237.7	24.92	210.8	19.67
6	[a]P-7	155.2	19.18	227.3	23.22		
7	[a]P-9	162.3	17.22	223.2	19.34		

T_{c1}, ΔH_{c1}/T_{c2}, ΔH_{c2} Crystal transition temperature and enthalpy in heating/cooling run.
T_m, ΔH_m Melting temperature and enthalpy.
[a] The quenched samples P-7, P-9 had not showed the cold crystallization in cooling run.

TABLE IV
Crystallization and Melting Behavior of the Samples Treated with Solvent

Composition		Heating Run				cooling Run	
Samples	SIP (mol) %	T_{c1} (°C)	$-\Delta H_{c1}$ (J/g)	T_m (°C)	ΔH_m (J/g)	T_{c2} (°C)	$-\Delta H_{c2}$ (J/g)
1	P-0	139.9	35.83	253.9	49.07	223.1	43.40
2	P-2	138.5	28.23	247.8	36.13	223.5	38.25
3	P-3	135.9	27.57	238.1	35.09	214.1	35.82
4	P-4	145.4	26.33	236.0	30.24	213.3	32.28
5	P-6	151.8	25.00	229.3	25.53	212.0	19.46
6	[a]P-7	153.7	19.78	221.4	23.30		
7	[a]P-9	156.8	17.48	215.0	21.39		

[a] P-7, P-9 samples treated with solvent had not showed the cold crystallization in cooling run.

of the heat of fusion was performed using the heat of fusion of indium and zinc. Runs were carried out with automatic baseline correction. The baseline was obtained by performing a heating run with no sample or via reference pans using a scan rate 10°C/min. The curvature of the baseline was minimized for the chosen temperature range. Pieces of around 10 mg were respectively taken from the dried samples, then put in a sample pan. The samples were tested under the dry nitrogen condition, a heating rate at 10°C/min, covering the range of 20–300°C, a cooling rate at 10°C/min, covering the range of 300–120°C. Repeating the first run after a series of runs, the same results are obtained with the same sample. The T_g was taken as the midpoint of the specific heat increment. The T_m, T_{c1}, and T_{c2} were taken as peak values of the respective endothermal or exothermal processes in the DSC curves. The results were respectively showed in Tables II, III, and IV.

RESULTS AND DISCUSSION

The T_g affected by the Na-SIP concentration was shown in Figure 2. The changes in glass transition temperature occurred on addition of Na-SIP to the
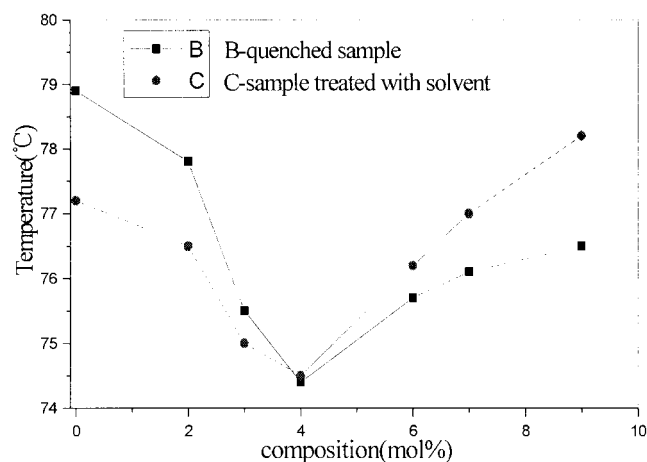

Figure 2 Effect of SIP content on glass transition temperature.

PET backbone. Under Na-SIPA levels ≤ 4 mol %, the T_g of the samples was down. This result is different from other related reports.[5] It is considered that the addition of a few of Na-SIP ionic moieties of the unsymmetrical structure weaken the symmetry of the PET structure, furthermore, increase the distance and the active space among macromolecular chains segments, which contribute to the segmental mobility of the polyester macromolecular chain and also play a plasticizer role in the polyester. With the further increase of Na-SIP concentration, at Na-SIP levels > 4 mol %, the strong polar sodium ions of ionic comonomer in the polymer macromolecules are attracted to the neighboring sulfonium ion in the ionized state. The ions in the unstable state have a tendency to form stable ion aggregates that act as simple thermoreversible crosslinks, which may be ion pairs aggregate (see Fig. 3) or higher aggregates, for example, quadruplets or sextuplets.[2] Electrostatic force applied by the ionic moieties induces the formation of these aggregates. Under Na-SIP levels ≤ 4 mol %, it is not enough to occur the aggregate and interaction among ionic groups because of lower ionic concentration and the distance between the ionic groups of the uniform dispersion formed with full stirring. These aggregates increase the effective molecular size of macromolecule significantly and effectively retard the translational mobility of the macromolecular chain segments, thereby leading to the glass transition temperature raising even though the molecular weight has de-
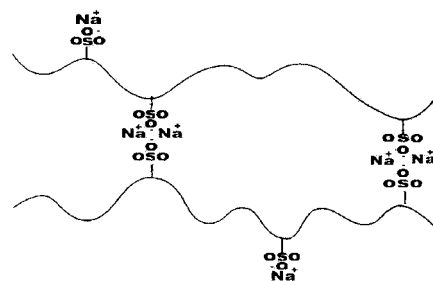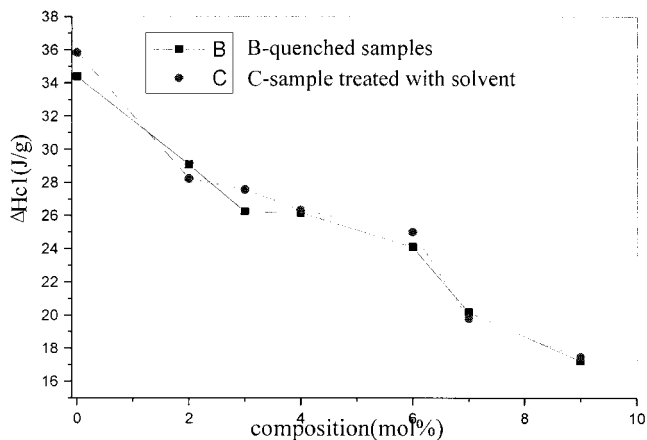

Figure 3 The aggregate of SIP ionic groups.

Figure 4 Effect of SIP on crystal enthalpy.

Figure 6 Effect of SIP on melting enthalpy.

creased.[5,6] As Figure 2 showed, the T_g of the P-6 had risen again. Although the T_g of the P-9 quenched samples are not significantly higher than those of the P-0 samples [due to its lower molecular weight, e.g. the IV(dL/g) of the P-9 sample is only 0.369, the P-0 is 0.690], the total tendency of the T_g is ascending. It may be considered that T_g is not affected by crystallization according to the enthalpy of crystallization; ΔH_{c1}, ΔH_{c2}, and melting ΔH_m. The samples treated either by quenching or dissolution was basically amorphous in the structure of the ionomeric polyester before testing. More experiments on the ionomeric polyester prove that the trace of the T_g cannot be found for the samples after the crystallization. Compared with sulfonates, the polarity of the ester functions is very low because there is the conjugated electron cloud in the ester covalent bond, which makes the polarity of the ester covalent bond weaken, then the Na^+ cannot be attracted by the ester functions. Furthermore, the ester functions are in the center of the polyester macromolecule chain; the polymeric space arrangement also obstructs interactions between the sulfonates and ester functions.
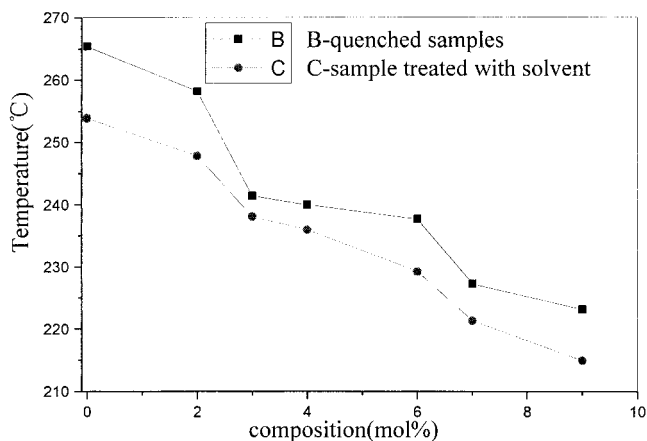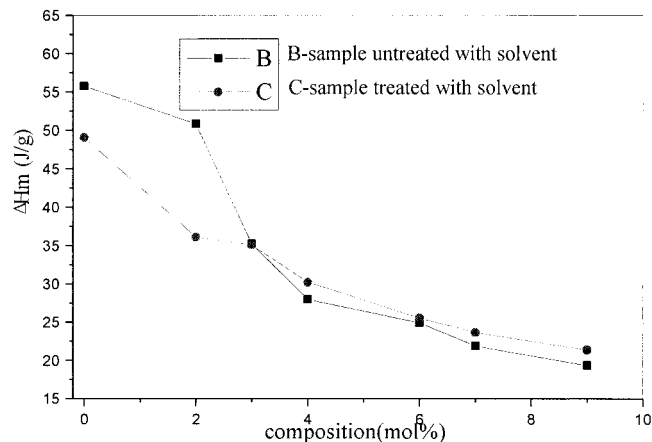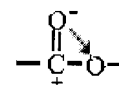
The addition of a few of the Na-SIP ionic moieties of the unsymmetrical structure decreased simultaneously, and the degree of crystallinity of the PET (the enthalpy of crystallization ΔH_{c1}, ΔH_{c2} was determined from DSC exothermal peaks (see Figs. 8 and 9). Usually, pure PET has a higher symmetrical structure in the macromolecular chain, which contributes to the crystallization of the polyester macromolecular; therefore, it has higher crystallinity[7] (the theoretical enthalpy of the crystallized completely PET is 105.5 J/g). The unsymmetrical moieties increase in the polymer structure, leading to a decrease of the crystal enthalpy ΔH_{c1}, ΔH_{c2} and melting enthalpy ΔH_m (see Table III, IV and Fig. 6).

The initiative crystal temperature, T_{c1}, showed the decline to the P-2, P-3 samples, which was similar to the T_g in the heating run and the T_{c2}, a slight hoist in the cooling run to the P-2 sample (see T_{c1}, T_{c2} in Tables III and IV and Figs.7, 8, and 9). This result, like the T_g, proved the plasticization of the few unsymmetrical

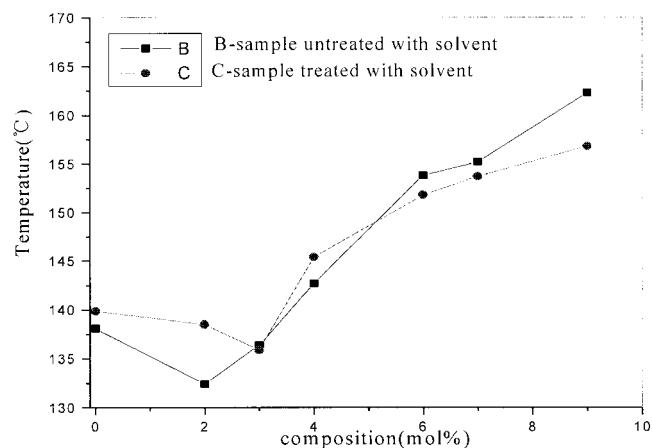**Figure 5** Effect of SIP on melting temperature.

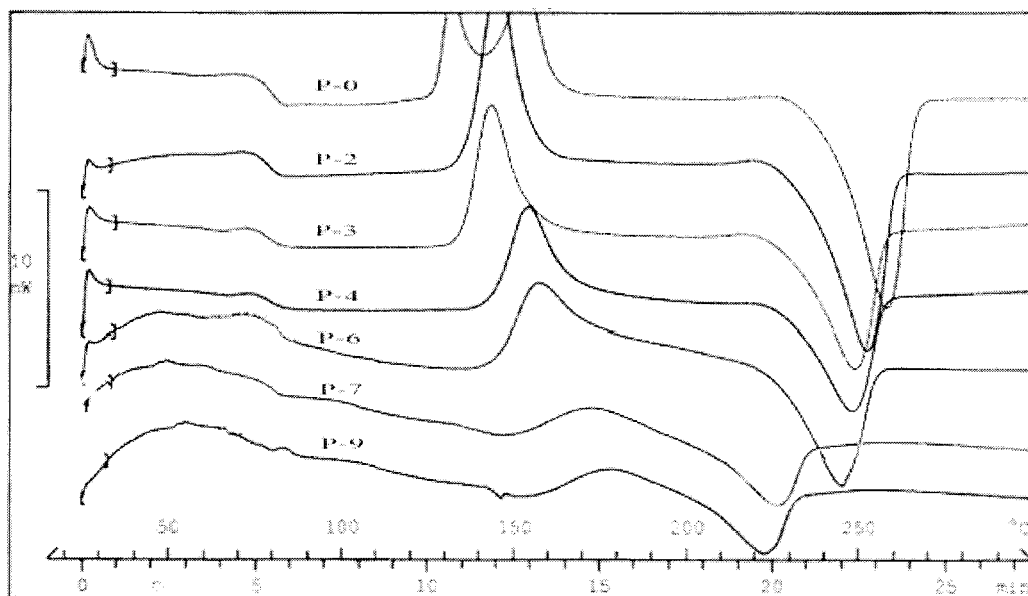**Figure 7** Effect of SIP on cold crystalization temperature.

Figure 8 DSC curves of the polyester ionomers in the heating run from 15 to 300°C. The weight of samples varies respectively from 15 to 20 mg.

Na-SIP ionic groups in the polyester; subsequently, the curve of the T_{c1} appeared an obvious hoist due to the interaction of the Na-SIP ionic groups. Although the plasticization contributes to the mobility of the polyester macromolecular chain, which is beneficial to crystallization, the crystal formation was obstructed by the Na-SIP units of the unsymmetrical structure, and the degree of crystallinity appeared to decline significantly. Such phenomena were explained by the decrease of the crystal and melting enthalpy with the increase of the Na-SIPA concentration in the polyester. Herein, the crystallization of the polyester ionomers is more sensitive to the concentration of ionic species, for the P-3 samples had risen again in the T_{c1} and declined

in the T_{c2}. Figures 8 and 9 shows another example of the Na-SIP polyester DSC traces obtained on reheating after quenching melts from 300°C; the same results, as aforesaid, were obtained under the same testing condition. Note that the P-0 itself shows two cold crystal peaks in the heating run, indicating crystal diversity, but P-2 to P-9 shows only one peak.

CONCLUSION

It has been established through the studies of the polyester ionomers that changes in glass transition temperature on addition of Na-SIPA to the PET backbone depended on the concentration of the Na-SIPA
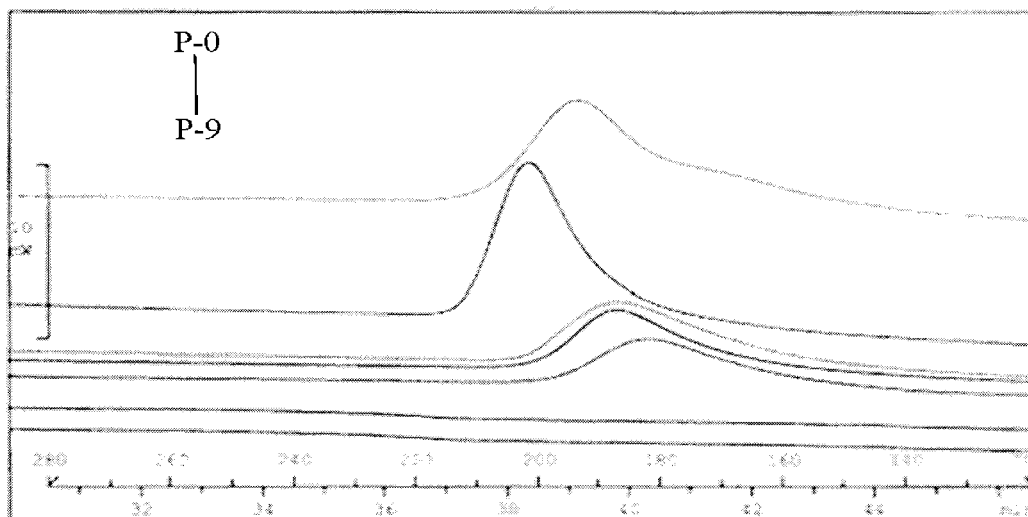

Figure 9 The DSC curves of the polyester ionomers in the cooling run from 300 to 120°C. The curves were obtained in the same experiments as in Figure 8

moieties. The dramatic effect of Na-SIPA on T_g is attributed to the formation of stable ionic aggregates. The T_g was not affected by crystallization according to the crystal enthalpy; ΔH_{c1}, ΔH_{c2}, and melting enthalpy; ΔH_m. The samples treated either by quenching or dissolution was basically amorphous in the structure of the ionomeric polyester before testing. The lower ionic concentration (at Na-SIPA levels $\leq$ 4 mol %) in ionomeric polyester was not enough for the the interaction among ionic groups to occur, which play only a plasticizer role in the polymer, thus, decreasing the glass transition temperature of the ionomeric polyester. At Na-SIPA levels > 4 mol %, the glass transition temperature of the ionomeric polyester comes to rise. The X = 4 mol % is considered as the tune point at which the aggregates generated by the interaction between ion–ion groups begin to form. The same results were obtained in all tested samples treated either by quenching or dissolution.

The plasticization of the Na-SIP made the crystal temperature T_{c1} of P-2, P-3 reduce, and T_{c2} hoist, but it is the space effect of the unsymmetrical Na-SIP structure for crystallization that plays a dominant role, which made the whole crystallization of the polyester ionomers bad. The changes of the cold crystal enthalpy and melting enthalpy as well as crystal temperature showed itself more difficult to crystallize with increasing the Na-SIP concentration.

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