Synthesis and Characterization of Telechelic Poly(ethylene terephthalate) Sodiosulfonate Ionomers

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ABSTRACT: Poly(ethylene terephthalate) (PET) ionomers containing terminal units derived from 3-sulfobenzoic acid, sodium salt (SSBA), were synthesized using metal-catalyzed melt polymerization techniques. SSBA (1.0−5.0 mol %) in the presence of sodium acetate (10 mol % compared to SSBA) served as an ideal chain-end functionalization reagent, and molecular weights ($\eta_{\mathrm{inh}} = 0.28-0.80$) were reproducibly obtained at various SSBA levels. ^{1}H NMR spectroscopy quantified the presence of the sodiosulfonate end groups and the formation of diethylene glycol. For comparative purposes, polyesters containing telechelic alkyl ester end groups derived from dodecanol were also synthesized at nearly equivalent molecular weights in order to fundamentally understand the role of ionic end groups on rheological and thermal performance. Differential scanning calorimetry indicated that the presence of ionic end groups significantly increased the crystallization half-time. A comparison of the crystallization half-time for telechelic ionomers vs non-ionomers demonstrated that ionic aggregation exerted a more profound effect in the diffusion-controlled regime (lower than 150 °C). Melt rheology confirmed that the ionic end groups increased the melt viscosity compared to non-ionomers at equivalent molecular weights. Moreover, ionomers and non-ionomers with nearly equivalent molecular weights exhibited similar slopes in log(melt viscosity) vs temperature curves, which is consistent with crystallization data. Melt viscosity vs temperature studies for telechelic ionomers also suggests that ionic aggregation was more stable below 150 °C compared to high molecular weight non-ionomer analogues.

Introduction

The presence of low concentrations of covalently bonded ionic substituents in organic polymers is known to exert a profound effect on their physical and rheological properties.[1−4] In fact, ionomers (polymers containing less than 20 mol % of ionic groups) have been shown to exhibit considerably higher moduli and higher glass transition temperatures compared to those of their nonionic analogues. Improvements in mechanical and thermal performance are generally attributed to the formation of ionic aggregates, which act as thermoreversible cross-links[1] and effectively retard the translational mobility of polymeric chains. The thermoreversible nature of ionic aggregation may address many other disadvantages associated with covalently bonded high molecular weight polymers, such as poor melt processability, high melt viscosity, and low thermal stability at typical processing conditions such as high shear rate and temperature. The precise form and size of these aggregates continue to receive significant attention, but their existence, as evidenced by small-angle X-ray scattering (SAXS), neutron scattering, and other techniques, is firmly established for many compositions.[4] Most investigations dealing with polyester ionomers have focused on random polyester ionomers, in which ionic groups were randomly distributed as pendant groups.[5−7] However, there are significantly fewer studies concerning telechelic polyester ionomers, where the ionic groups are located at the polymer chain ends.[8−10] Telechelic ionomers are generally recognized as model systems for random ionomers since the molecular weight between ionic end groups is controlled and the ionic groups are located exclusively at the polymer chain ends.[10] In addition, telechelic association, coupled with adjacent ordered sequences, serves to strengthen subsequent noncovalent association.[11−14] Telechelic ionic bonding using metal sulfonates is known to strongly associate in the solid state as ionic aggregates and are subsequently disrupted at elevated temperatures.

The relationship between ionic aggregation and crystallization remains an important topic in polymer science. Early investigations of semicrystalline ionomers have focused on polyethylene-based systems.[16] Recently, Moore and co-workers have investigated the crystallization behavior of lightly sulfonated syndiotactic polystyrene in more detail.[17−19] These workers demonstrated that ionic interactions altered the crystallization kinetics and resulting morphology, and decreased levels of crystallinity were observed. However, Moore concluded that the effect of ionic interactions on crystalline behavior may be partially due to the random incorporation of noncrystallizable repeating units into the polymer backbone, and more research was required to understand these interactions. Thus, telechelic ionomers provide the opportunity for electrostatic interactions without a deleterious effect on the symmetry of the repeating unit. Other workers have recently demonstrated that the addition of nucleating agents resulted in the formation of metal carboxylate end groups, which increased the crystallization rate.[20,21] It was proposed that ionic aggregation in the polymer melt will serve as a nucleation site. To more fully understand the crystallization behavior of semicrystalline ionomers without disruption of the repeat unit structure, PET telechelic ionomers with a high concentration of sul-

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fonate end groups and well-defined molecular weights were investigated.

PET crystallization kinetics are also dependent upon many other factors. Gunther and Zachmann[22] have investigated the effects of residual catalyst metals on the crystallization half time ($t_{1/2}$) and on PET orientation. Using identical film drawing conditions, an increase in the concentration of the residual catalyst system resulted in an increase in the degree of orientation. Although many catalyst metals including tin, titanium, manganese, and cobalt have been employed earlier for polyester processes, the influence of residual antimony metal catalyst more significantly influenced the crystallization rate.[23−26] However, a detailed mechanism that defined the origin of higher crystallization rates has not been proposed. Moreover, Jabarin and coworkers have also noted in some cases that the residual catalyst metal may exert a more significant effect on crystallization rate than polymer molecular weight. Diethylene glycol (DEG), which is formed as a byproduct during PET synthesis, has also been found to affect crystallization kinetics.[27−30]

This paper focuses on the synthesis and characterization of telechelic polyester ionomers using monofunctional 3-sulfobenzoic acid, sodium salt (SSBA). Special attention was devoted to the determination of the effect of terminal ionic groups and residual catalyst metals on the crystallization kinetics, melt rheology, and thermal transitions. In addition, dodecanol-terminated polyester oligomers were prepared for direct comparison at nearly equivalent molecular weight. A more detailed investigation of the morphology of the telechelic polyester ionomers will be reported in a future publication.

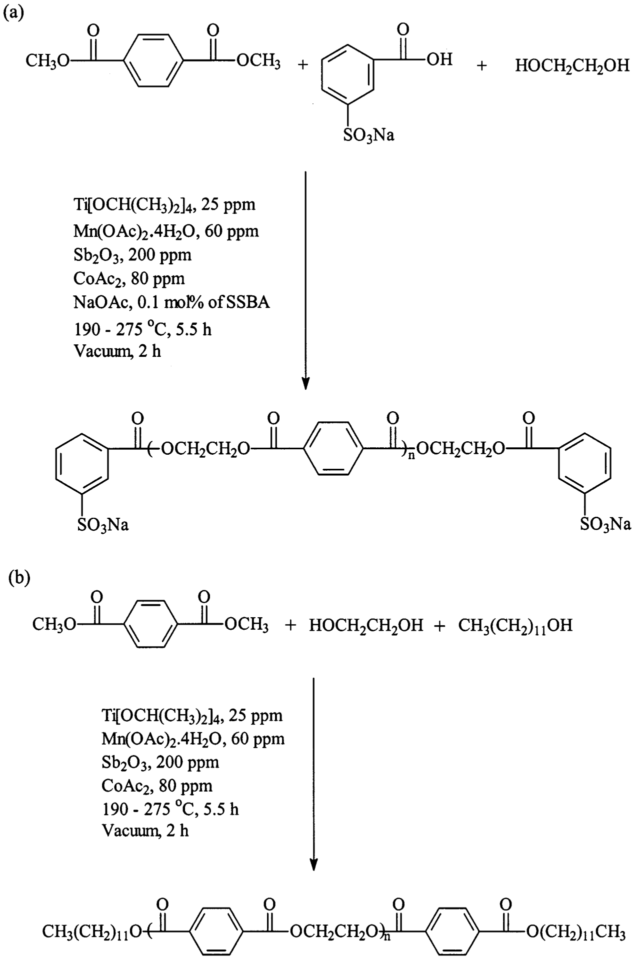
Experimental Section

Reagents. All monomers and reagents were used without further purification. Ethylene glycol (EG) and 3-sulfobenzoic acid, sodium salt (SSBA, 97%), were generously provided by Eastman Chemical Co. Dimethyl terephthalate (DMT), sodium acetate (ACS reagent grade, 99.5+%), and 1-dodecanol (DD) were purchased from Aldrich and used as received. Phosphoric acid (crystals, 98%), cobalt acetate (99%), antimony(III) oxide (99%), manganese acetate (99%), and titanium tetra(isopropoxide) were purchased from Aldrich and used as received.

Preparation of Catalyst Solutions. (a) Sb catalyst: Sb_2O_3 (3.00 g, 0.01 mol) solid was dissolved in 250 mL of ethylene glycol (EG). The mixture was heated at 100 °C and stirred for 24 h under nitrogen purge. The mixture was then filtered, and a clear solution was obtained at a concentration of 0.080 mol/L based on Sb. (b) Mn catalyst: $Mn(OAc)_2 \cdot 4H_2O$ (2.685 g, 0.011 mol) and glacial acetic acid (1.319 g, 0.022 mol) were added to 125 mL of EG and heated to form a catalyst solution at a concentration of 0.088 mol/L based on Mn. (c) Ti catalyst: The catalyst solution was obtained by mixing titanium isopropoxide (3.8 mL, 3.65 g, 0.013 mol) with 62.5 mL of 1-butanol in a dry bottle under nitrogen at a concentration of 0.196 mol/L based on Ti. (d) Co catalyst: Cobalt acetate (2.025 g, 0.011 mol) was mixed with EG (125 mL) to obtain a catalyst solution with a concentration of 0.088 mol/L based on Co. (e) P catalyst: Phosphoric acid (99%, 3.48 g, 0.036 mol) was dissolved in 1-butanol (12.5 g, 15.43 mL) and then mixed with EG (125 mL) to obtain catalyst at a concentration of 0.256 mol/L based on P.

Synthesis of Sulfonate-Terminated Telechelic Semicrystalline PET Ionomers (PET-*x*SSBA, Where *x* = the mol % of SSBA in the Polyester). To a mixture of dimethyl terephthalate (DMT, 48.5 g, 0.25 mol) and ethylene glycol (EG, 31 g, 0.5 mol, 100% excess), various amounts of end-capper, SSBA (x = 1, 3, 5, and 10 mol % compared to DMT), were added to obtain PET telechelic ionomers (Scheme 1a). Three series were prepared using different catalyst systems. The first series was synthesized with manganese catalyst (2.31 mL, 60 ppm), titanium catalyst (0.51 mL, 25 ppm), cobalt catalyst (3.0 mL, 80 ppm), and antimony catalyst (3.8 mL, 200 ppm), and finally, just prior to the vacuum, phosphoric acid (2.1 mL, 80 ppm) was added. The second series was synthesized in a similar fashion; however, manganese (2.31 mL, 60 ppm), antimony (3.8 mL, 200 ppm), and titanium (0.51 mL, 25 ppm) catalysts were used. The third series was prepared using manganese (2.31 mL, 200 ppm) and titanium (0.51 mL, 25 ppm) catalysts only. A multistep temperature procedure was used for all polymerizations; i.e., the reaction mixture was heated and stirred at 190 °C for 2 h, 220 °C for 2 h, and 275 °C for 0.5 h. Vacuum (0.5 mmHg) was applied for an additional 2 h. NaOAc was used in all polymerizations containing SSBA to quantitatively maintain the sulfonic acid in the sodium salt form. A constant 0.10:1.0 mole ratio of NaOAc to SSBA was maintained.

Scheme 1. (a) Synthesis of PET-*x*SSBA Ionomers Using Melt Polymerization; (b) Synthesis of PET-*y*DD Using Melt Polymerization



Synthesis of Dodecanol-Terminated Semicrystalline PET (PET-*y*DD, Where *y* = the mol % of Dodecanol in the Polyester). To a mixture of dimethyl terephthalate (48.5 g, 0.25 mol) and ethylene glycol (31 g, 0.5 mol, 100% excess), various amounts of dodecanol (5, 10, 12, and 15 mol %) were added (Scheme 1b). Correspondingly, the same three series were prepared using different catalyst systems as mentioned above. The same multistep temperatures were also used for the reaction; i.e., the reaction mixture was heated and stirred at 190 °C for 2 h, 220 °C for 2 h, and 275 °C for 0.5 h. At the end, vacuum (0.5 mmHg) was applied for an additional 2 h. No further purification was needed.

Polymer Characterization. 400 MHz NMR (Varian-400) spectroscopy in trifluoroacetic acid (TFA)/$CDCl_3$ (2:1, v/v) was used to characterize polyester composition and end groups.

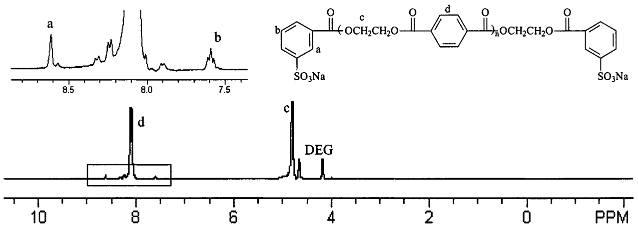


Figure 1. ^{1}H NMR spectrum of PET-5%SSBA, $CF_3COOD/CDCl_3$, 2:1 (v/v), room temperature.

FTIR spectra were collected on an infrared spectrometer (Perkin-Elmer, 283B) to confirm the presence of the sulfonate end groups. Gel permeation chromatography (GPC) was performed to obtain molecular weights and molecular weight distributions using a Waters 2690 chromatograph equipped with a differential refractive index detector (Viscotek Laser refractometer) and an on-line differential viscometric detector (Viscotek 100) coupled in parallel, using polystyrene standards. Phenol/tetrachloroethane (60/40, w/w) was utilized as the mobile phase, and the data were recorded at 25 °C at a flow rate of 1.0 mL/min. Melt rheology was analyzed using a melt rheometer (TA Instruments, advanced rheometer AR 1000) under nitrogen. DSC (Perkin-Elmer, Pyris 1) was used to study glass transition temperatures and crystallization behavior. All the samples were maintained at 290 °C for 3 min to eliminate any thermal history, then quenched from 290 °C to room temperature at a rate of 200 °C/min, and finally ramped to 290 °C at a rate of 10 °C/min. All DSC experiments were performed under nitrogen. The solution behavior of the samples was studied using an Ubbelohde viscometer at 25 ± 0.1 °C in phenol and tetrachloroethane (60/40, w/w).

Crystallization Studies. DSC (Perkin-Elmer, Pyris 1) was used to study the isothermal crystallization behaviors of the polyesters. All samples were dried (150 °C, 4−6 h) in a vacuum oven (1.0 mmHg) prior to analysis. A typical procedure is described below. A sample (~10 mg) was weighed in an aluminum DSC sample pan. The calorimeter was operated with a steady stream of oxygen-free, dry nitrogen throughout the experiment. The sample was heated at a rate of 25 °C/min to 290 °C and held for 20 min. The sample was rapidly quenched at 200 °C/min to the isothermal crystallization temperature and maintained at this temperature for 45 min to reach thermal equilibrium and ensure that crystallization was complete. The entire procedure was repeated for a series of isothermal crystallization temperatures, and crystallization curves at various crystallization temperatures were collected. In each case, a new sample was utilized for each isothermal crystallization temperature, and duplicate measurements ensured reproducibility. Crystallization windows, i.e., half-time of crystallization vs temperature, were constructed and used for comparative purposes.

Results and Discussion

Chemical Composition and Molecular Weight Control. Figure 1 depicts the NMR spectrum for PET-5%SSBA. Resonances at 8.1 ppm (aryl hydrogens (d)) and 4.8 ppm (aliphatic hydrogens (c)) are associated with the repeating unit, and resonances at 8.6 and 7.6 ppm are associated with the aryl hydrogens in the SSBA end group. Table 1 indicates that SSBA incorporation was quantitative, and the SSBA charge agreed well with the SSBA concentration in the polyester as determined using ^{1}H NMR. In addition, these data confirmed that the SSBA was not volatile during the polymerization process, and SSBA was not detected in the polymerization condensate. Furthermore, number-average molecular weights were determined using ^{1}H NMR based on SSBA resonances (Table 1). ^{1}H NMR was also utilized to ascertain DEG levels (Table 4), and resonances at 4.15 ppm ($OCH_2C\mathit{H}_2OC\mathit{H}_2CH_2O$) and 4.55 ppm ($OC\mathit{H}_2CH_2OCH_2C\mathit{H}_2O$) were assigned to the DEG sequence.[31] NaOAc ensured that the DEG levels were reproducibly lower than 3 mol %. In a fashion similar to poly(ethylene isophthalate) SSBA telechelic ionomers,[32,33] an absorbance associated with the S−O stretching mode was observed at 630 cm^{-1}, and a linear relationship existed between the mol % SSBA charged and mol % SSBA that was present in the telechelic polyester ionomer.[34]

^{1}H NMR was also used to confirm the polymer composition and end groups for PET-*y*DD polyesters. Figure 2 depicts the ^{1}H NMR spectrum for PET-5%DD, and as expected on the basis of PET-*x*SSBA repeating unit assignments, the aryl hydrogens appeared at 8.2 ppm (4H, s) and the aliphatic hydrogens appeared at 4.9 ppm (4H, s). Dodecanol end groups were assigned at 4.5 ppm (H_a, t), 1.9 ppm (H_b, m), 1.4 ppm (H_c, m), and 0.9 ppm (H_d, t). ^{1}H NMR confirmed that the level of incorporated dodecanol was significantly lower than the dodecanol feed, and dodecanol was confirmed in the polymerization condensate. Dodecanol distilled during polymerization (275 °C) due to its relatively low boiling temperature (260−262 °C).Table 2 summarizes the level of dodecanol incorporation vs the mol % charged. It is clear that a majority of the charged dodecanol is lost during polycondensation; however, GPC analysis, as described below, indicates that the molecular weight control is reproducible for various levels of dodecanol.

Although GPC was not possible for the SSBA telechelic ionomers due to interactions with the chromatographic columns, GPC was successfully utilized to obtain the molecular weights and molecular weight distributions for PET-*y*DD. The M_w/M_n values for various PET-*y*DD samples were reproducibly between 2.2 and 2.5, which was expected for a traditional polycondensation. An inverse correlation (Figure 3) was observed between the amount of dodecanol charged and the number-average molecular weight. The reproducible linear relationship between number-average molecular weight and the mol % dodecanol that was charged permitted predictable number-average molecular weights of PET-*y*DD. The utility of this linear relationship is a function of the well-defined polymerization conditions and may vary depending on selected temperature profiles and ultimate vacuum levels.

Since excess ethylene glycol was used in the polymerization methodology and subsequently was removed by distillation during polycondensation, the conventional equation, $X = (1 + r)/(1 - r)$, was not applicable. Assuming that the end-capping reaction was quantitative and restricted to the polymer chain end, a modified equation (eq 1) was utilized to estimate the theoretical number-average molecular weights. Table 3 includes the theoretical number-average molecular weights for the PET-*x*SSBA ionomers.

$$\begin{aligned}\langle M_n\rangle &= (\text{total mass of product molecules})/\\ &\qquad (\text{moles of product molecules})\\ &= [\textstyle\sum(m_e + x m_{ru})]/(N(\mathrm{A})/2) \qquad (1)\end{aligned}$$

where m_e is the molar mass of the combined end groups, m_{ru} is the molar mass of an internal repeat unit, N(A) is moles of monofunctional end-capping reagent, and x is the number of internal repeat units.

Table 1. NMR Analysis of SSBA-Terminated PET Oligomers

sample	catalysts	charged SSBA (mol %)	SSBA in polymer (mol %)	CH_3 end group in polymer (mol %)	DEG (mol %)	M_n (g/mol)
PET-3%SSBA	Ti/Mn/Sb/Co/P	3.00	2.91	0.11	2.9	13100
PET-5%SSBA	Ti/Mn/Sb/Co/P	5.00	4.80	0.19	3.2	8300

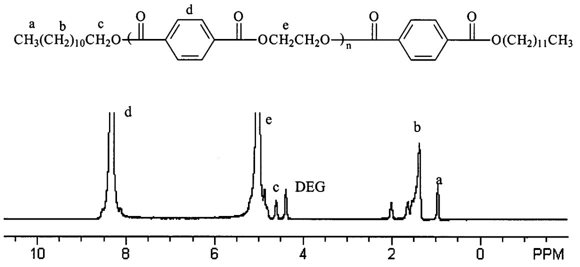


Figure 2. ^1H NMR spectrum of PET-5%DD, CF_3COOD/$CDCl_3$, 2:1 (v/v), room temperature.

Table 2. GPC Analysis of PET-*y*DD with Various Amounts of Dodecanol; Solvent: Phenol/Tetrachloroethane (60/40, w/w)

PET-*x*DD	mol % dodecanol charged	residual DD (mol %)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
PET-1%DD	5	1.25	23 300	57 300	2.46
PET-2%DD	10	2.33	16 500	35 800	2.21
PET-3%DD	12	3.12	13 100	28 800	2.20
PET-5%DD	15	5.08	8 100	19 300	2.14

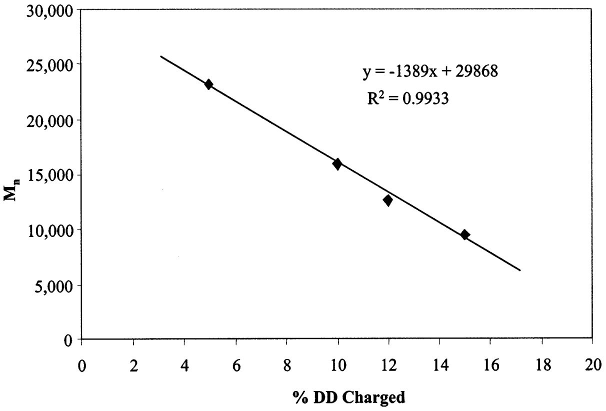


Figure 3. Number-average molecular weight vs percentage of charged dodecanol in the synthesis of PET-*y*DD.

Solution viscometry was used to study the dilute solution behavior of the polyester telechelic ionomers and dodecanol-terminated oligomers. The preferred solvent was a mixture of phenol and tetrachloroethane (60/40, w/w, 25 °C). PET-5%SSBA samples exhibited upward curvatures in the Huggins and Kreamer equations. Nonlinear relationships between solution viscosity and dilute polymer concentration are characteristic behaviors of ionomers and are believed to arise from ionic interactions in solution.[32,35] Dodecanol-terminated polyesters, PET-*y*DD, were also analyzed, and linear relationships were observed for the Huggins and Kreamer equations over a similar dilute solution concentration range.

Thermal Transitions and Crystallization Behavior. DSC analysis indicated that the low molecular weight ionomers (PET-3%SSBA and PET-5%SSBA) exhibited similar thermal transition to high molecular weight PET, and distinct glass, crystallization, and melt transitions were observed (Table 3). In contrast, dodecanol-end-capped, low molecular weight polyesters (8000 g/mol) exhibited typical thermal transitions as low molecular weight polyesters, and only a melt transition was observed due to more rapid crystallization during the quenching process from 290 °C. Moreover, as the sulfonate end group concentration increased from 0 to 5 mol %, the crystallization temperature upon heating (T_c) increased from 137 to 151 °C and the T_m decreased form 244 to 213 °C (Table 3). These observations suggest that the presence of ionic aggregation restricted polymer mobility and hindered crystallization processes. Moreover, ionic interactions also significantly influenced the stability of the crystalline phase and resulted in the formation of a crystalline phase that contained more defects. However, in contrast to random ionomers,[17−19] the dodecanol-terminated and telechelic ionomers exhibited a similar heat of fusion (Table 3). This observation also indicates that the ionic end groups and any associated ionic aggregation did not significantly influence the level of crystallinity.

To quantitatively determine the effect of ionic aggregation on the crystallization kinetics, isothermal crystallization studies at different temperatures were performed. Because of the rapid crystallization rate for low molecular weight PET-5%DD, it was experimentally difficult using differential scanning calorimetry to measure the crystallization half-time. Thus, direct comparisons between nearly equivalent molecular weight telechelic ionomers and dodecanol-terminated oligomers were not performed. Higher molecular weight PET-2%DD ($M_n = 16\,500$) was selected for comparison to PET-5%SSBA ($M_n = 8100$). The crystallization half-time vs temperature curves for PET-5%SSBA and PET-2%DD are depicted in Figure 4a. Higher polyester molecular weights typically resulted in a reduced crystallization rate; however, despite the higher molecular weight, the crystallization rate of PET-2%DD was significantly higher than PET-5%SSBA. In contrast, earlier observations for PET ionomers that contained low levels of ionic end groups[20,21] resulted in increased crystallization rates.

The isothermal crystallization data were also analyzed using the Avrami equation,[36]

$$\ln[-\ln(1 - X_t)] = \ln K + n \ln t \tag{2}$$

where X_t is the weight fraction of the crystalline component at time t, K is the kinetic growth constant, and n is the Avrami exponent. The n values for both telechelic ionomers and non-ionomers were determined to be in the 2.7−3.2 range. (The linear regression correlation coefficients, r^2, were typically 0.98.) These results suggest that although the crystallization rate was retarded due to the presence of ionic aggregation, the principal mechanism for crystallization of both telechelic ionomers and non-ionomers was similar.

Previous investigations dealing with the crystalline behavior of poly(ethylene) random ionomers and poly(styrene) random ionomers demonstrate that the effect of ionic interactions on crystallization rate was temperature-dependent.[17−19] Counterion experiments suggest that, in the interfacial-controlled region, the ionic groups were able to hop among multiplets easily, and the

Table 3. DSC Analysis of Nonterminated PET, PET-*x*SSBA, and PET-*y*DD, N_2, Second Heat with Heating Rate at 10 °C/min

polymers	M_n (g/mol)	T_g (°C)	T_c (°C)	Δ (J/g)	T_m (°C)	Δ (J/g)
nonterminated PET	24 800	77	137	30.4	244	45.4
PET-1%SSBA	23 600	78	142	33.5	234	47.2
PET-3%SSBA	13 400	76	147	27.0	231	45.3
PET-5%SSBA	8 200	77	151	32.6	212	43.3
PET-1%DD	23 300	75	147	29.2	243	48.1
PET-2%DD	16 500	70	132	18.2	244	46.2
PET-5%DD	8 100				249	47.0

Table 4. Composition, Inherent Viscosity, and Catalyst Composition of PET-*y*DD and PET-*x*SSBA Samples That Were Used in Isothermal Crystallization Studies

samples	catalysts	η_{inh}	DEG (%)
PET-5%SSBA	Ti/Mn/Sb/Co/P	0.282	3.2
PET-2%DD	Ti/Mn/Sb/Co/P	0.556	3.0
PET-5%DD	Ti/Mn/Sb/Co/P	0.281	2.9
PET-2%DD$_{(Ti/Mn)}$	Ti/Mn	0.553	2.7
PET-2%DD$_{(Ti/Mn/Sb)}$	Ti/Mn/Sb	0.551	2.8
PET-5%SSBA$_{(Ti/Mn)}$	Ti/Mn	0.283	3.3
PET-5%SSBA$_{(Ti/Mn/Sb)}$	Ti/Mn/Sb	0.281	3.1

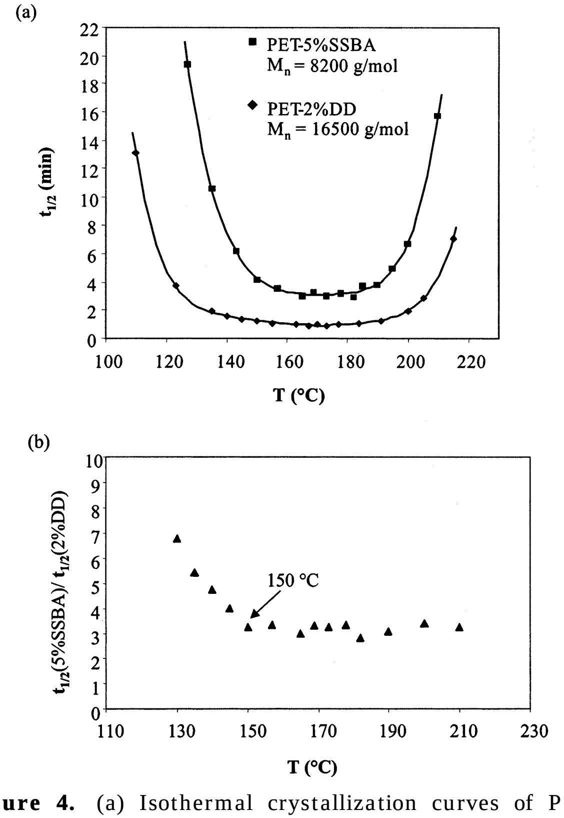


Figure 4. (a) Isothermal crystallization curves of PET-5%SSBA and PET-2%DD. (b) Ratio of the crystallization half times of ionic PET-5%SSBA and PET-2%DD as a function of temperature.

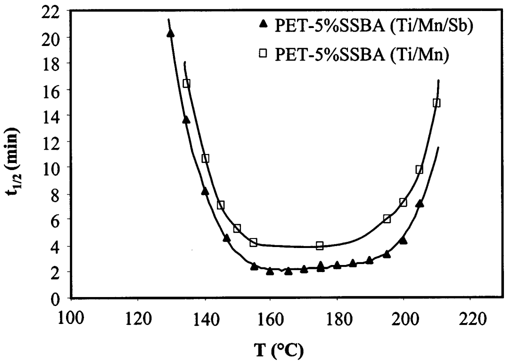


Figure 5. Isothermal crystallization curves for PET-5%SSBA$_{(Ti/Mn)}$ and PET-5%SSBA$_{(Ti/Mn/Sb)}$.

relaxation of ionic aggregates was on the same time scale as crystallization.[17-19] However, in the diffusion-controlled region, ionic aggregation was more stable, and the relaxation times for ionic aggregates were significantly longer. To study the effect of ionic aggregation in PET telechelic sodium salt ionomers on the crystallization behavior in different regions, the half-time ratio ($t_{1/2}$(PET-5%SSBA)/$t_{1/2}$(PET-2%DD)) was calculated and analyzed as depicted in Figure 4b. Figure 4b revealed that the crystallization half-time ratio was temperature-dependent before 150 °C (diffusion-controlled region) and remained relatively constant above 150 °C (interfacial-controlled region). This observation suggests that in the diffusion-controlled region the decrease in the relaxation time for the ionic aggregates with an increase in temperature was obvious, and local chain mobility dramatically increased with an increase in temperature. However, at temperatures that exceeded 150 °C, the activation energy for ion hopping was small, and a temperature increase did not further facilitate the disruption of the ionic aggregates. These observations were consistent with Moore et al., who performed counterion studies on lightly sulfonated syndiotactic polystyrene.[17-19]

Catalyst residues, especially residual antimony metal, have a significant effect on the crystallization rate.[23-26] In particular, residual antimony was shown earlier to increase crystallization rate. The residual antimony catalyst is not covalently bound to the polyester backbone, and quantitative extractions were possible using acetic acid without molecular weight loss or compositional changes. The isothermal crystallization behavior of PET-5%SSBA$_{(Ti/Mn)}$ and PET-5%SSBA$_{(Ti/Mn/Sb)}$ was investigated to determine the effect of residual antimony catalysts on the crystallization of telechelic ionomers. Figure 5 depicts the $t_{1/2}$ vs temperature for these two polyesters that contain different catalyst metals, but nearly equivalent molecular weights ($\eta_{inh} \sim 0.28$) and DEG levels (~3 mol %) within experimental error. It was evident that the $t_{1/2}$ for crystallization of PET-5%SSBA$_{(Ti/Mn/Sb)}$ was less than PET-5%SSBA$_{(Ti/Mn)}$ at the same temperature, indicating that PET-5%SSBA$_{(Ti/Mn/Sb)}$ exhibited a higher crystallization rate compared to PET-5%SSBA$_{(Ti/Mn)}$. Complementary melt rheological investigations were performed to further understand the role of residual antimony catalyst (Figure 6a,b) on thermal transitions. Figure 6a illustrates that the transition temperature for viscous flow (T_{flow}) for PET-5%-SSBA$_{(Ti/Mn/Sb)}$ was 20 °C higher than PET-5%SSBA$_{(Ti/Mn)}$. Both telechelic ionomers had inherent viscosities within experimental error ($\eta_{inh} \sim 0.28$). To elucidate the influence of residual antimony, dodecanol-terminated oligomers were also investigated as a function of antimony content. Figure 6b depicts the viscosity vs temperature profiles for nearly equivalent inherent viscosity ($\eta_{inh} \sim 0.55$) PET-2%DD$_{(Ti/Mn)}$ and PET-2%DD$_{(Ti/Mn/Sb)}$.

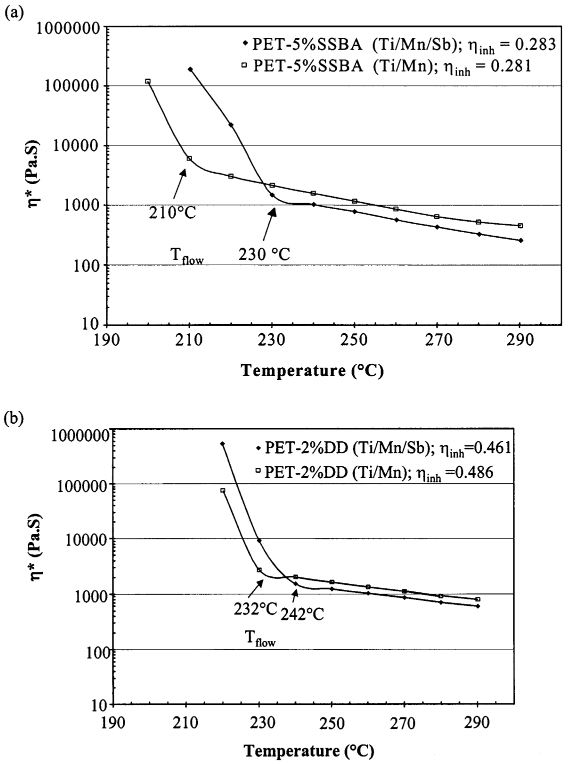


Figure 6. (a) Melt rheology of PET-5%SSBA with and without antimony trioxide catalyst. (b) Melt rheology of PET-2%DD with and without antimony catalyst.

The transition temperature to viscous flow was 242 °C for PET-2%DD$_{(Ti/Mn/Sb)}$ and 232 °C for PET-2%DD$_{(Ti/Mn)}$. As suggested earlier in the literature, the 10 °C difference may be attributed to nucleation of the residual antimony catalyst, resulting in different levels of crystallinity. This more significant influence of the residual antimony catalyst on the thermal transition temperatures of telechelic ionomers suggests that residual antimony may function as a nucleating agent. Thus, the residual antimony catalyst metal served to balance the disruptive effects of ionic aggregation on the crystallization rate.

Melt Rheological Analysis. To quantitatively ascertain the effect of ionic aggregation on polymer chain mobility, the melt rheological performance of ionomers and non-ionomers was measured. A comparison of parts a and b of Figure 6 reveals that telechelic ionomers exhibited a higher melt viscosity compared to that of dodecanol-terminated polyesters over the entire temperature range due to ionic aggregation in melt state. Further investigations of PET-*y*DD also revealed that the melt viscosity at 250−290 °C decreased with an increase in dodecanol content (Figure 7). This was expected on the basis of lower GPC molecular weights and solution viscosities. In addition, it was observed that T_{flow} increased with a decrease in molecular weight. As expected, based on our DSC studies and earlier literature,[37−39] the lower molecular weight polyesters resulted in more facile crystallization. Moreover, ionomers and non-ionomers exhibited similar slopes in the log(melt viscosity) vs temperature profile. However, in our previous studies dealing with amorphous telechelic polyester ionomers, the effect of temperature on the melt viscosity was more pronounced at lower temperatures (<150 °C).[33] These earlier melt rheological observations further support the relationship of temperature and crystallization rate for poly(ethylene terephthalate)-based telechelic ionomers.

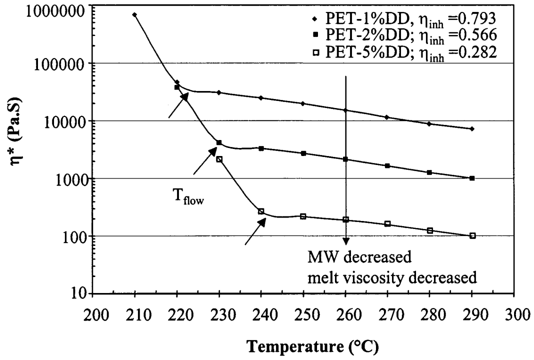


Figure 7. Melt viscosity vs temperature for PET-1%DD, PET-2%DD, and PET-5%DD.

Conclusions

Poly(ethylene terephthalate) containing either sodiosulfonate or dodecanol end groups were prepared using melt polymerization methodologies. ^{1}H NMR spectroscopy confirmed the chemical composition, end-group structure, and number-average molecular weights. GPC and solution viscosity measurements were also used to determine molecular weights and permitted an investigation of the influence of molecular weight and end-group structure on the thermal and rheological performance. Ionic aggregation decreased the crystallization rate due to retarded polymer chain mobility. Isothermal crystallization studies and rheological analysis suggest that, at temperatures exceeding 150 °C, the ionic groups were able to hop at a high rate, and that the increased temperature did not further disrupt the ionic aggregation. Melt rheological investigations and crystallization rate studies also indicate that a residual antimony catalyst was able to partially compensate for the disruptive effect of ionic aggregation.

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