Synthesis and Characterization of Elastoplastic Poly(styrene-*co*-ethylene) Using Novel Mono(η^5-cyclopentadienyl) titanium and Modified Methylaluminoxane Catalysts

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ABSTRACT: Elastoplastic poly(styrene-*co*-ethylene) with high molecular weight was synthesized using novel mono(η^5-pentamethylcyclopentadienyl)tribenzyloxy titanium [Cp*Ti(OBz)$_3$] complex activated with four types of modified methylaluminoxanes (mMAO) containing different amounts of residual trimethylaluminum (TMA). The ideal mMAO, used as a cocatalyst for the copolymerization of styrene with ethylene, contains TMA approaching to 17.8 wt %. The oxidation states of the titanium-active species in different Cp*Ti(OBz)$_3$/mMAO catalytic systems were determined by the redox titration method. The results show that both active species may exist in the current system, where one [Ti(IV)] gives a copolymer of styrene and ethylene, and the second one [Ti(III)] only produces syndiotactic polystyrene (sPS). Catalytic activity, compositions of copolymerization products, styrene incorporation, and copolymer microstructure depend on copolymerization conditions, including polymerization temperature, Al/Ti, molar ratio, and comonomers feed ratio. The copolymerization products were fractionated by successive solvent extractions with boiling butanone and tetrahydrofuran (THF). The copolymer, chiefly existing in THF-soluble fractions, was confirmed by ^{13}C-NMR, GPC, DSC, and WAXD to be an elastoplastic copolymer with a single glass transition temperature. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1851–1857, 1999

Key words: metallocene catalyst; methylaluminoxane; copolymer of styrene and ethylene; syndiotactic polystyrene; polyethylene

INTRODUCTION

Currently, mono(η^5-cyclopentadienyl)titanium complexes activated by MAO for syndiospecific polymerization of styrene are well known,[1–5] as well as for the polymerization of ethylene[6,7] and propylene.[8,9] The active species of mono(η^5-cyclopentadienyl)titanium/MAO catalyzing different monomers have been analyzed by various methods. The results show that Ti(III) active species favor production of syndiotactic polystyrene,[10,11]

and Ti(IV) complexes contribute as the active species to ethylene and propylene atactic polymerization.[12,13]

Copolymerization of styrene with ethylene, based on metallocene catalysts, has attracted considerable attention in recent years.[14–21] Depending on the polymerization conditions and the catalyst composition and structure, alternating, block, and pseudorandom styrene/ethylene copolymers can be produced. Longo et al.[22] found that, using CpTiCl$_3$ and MAO as catalysts for styrene and ethylene copolymerization, a MAO/Ti ratio of 1000 produced a block copolymer while, with a ratio of 100, polyethylene bridged by styrene was produced. However, Seppala et al.[23,24] also exam-

ined the copolymerization of styrene with ethylene by titanium compounds with bulky alkoxy ligands and also CpTiCl$_3$ and MAO. The products of the polymerization did not contain a true copolymer but a mixture of polyethylene and syndiotactic polystyrene. They suggested that there are more than two active species in this catalyst system. Ichihara et al.[25] prepared a crystalline styrene and ethylene copolymer with the Cp*Ti(OMe)$_3$ and MAO catalyst systems, in which the styrene chain has a syndiotactic configuration. Lin et al.[26] reported that the Cp*Ti(OPh)$_3$/MAO catalyst produced an elastoplastic and amorphous copolymer of styrene and ethylene. It was found that external addition of trimethylaluminum or tri-iso-butyluminum inhibited the copolymerization but promoted styrene homopolymerization. They analyzed the oxidation states of the titanium in Cp*Ti(OPh)$_3$/MAO catalyst systems with toluene as a solvent by ESR spectroscopic, and suggested a cationic Ti(III) active species-produced sPS, and Ti(IV) active species-produced polyethylene (PE). Styrene and ethylene copolymerization proceeded via a third intermediate active species. Alternating styrene/ethylene copolymers prepared using C_s symmetric metallocene complexes activated by MAO have been reported.[27] Recently, metallocene catalysts with constrained ligand geometry have been used for copolymerization of styrene and ethylene.[28] ^{13}C-NMR spectroscopic microstructure analysis showed exclusively tail-to-tail coupling of styrene units in the polymer backbone.

The random styrene/ethylene copolymer produced with half-sandwich metallocene and MAO catalysts mentioned above literature,

have no head-to-tail styrene–styrene sequences. In this article, we report on several modified methylaluminoxanes (mMAO) containing different percentage contents of TMA that were used as the cocatalysts to activate Cp*Ti(OBz)$_3$ for styrene and ethylene copolymerization. It is found that the content of residual trimethylaluminium (TMA) in mMAO has an important influence on the formation of active species for producing styrene and ethylene copolymer. The copolymers were composed of ethylene segments, isolated styrene units, alternating styrene–ethylene sequences, and not only tail-to-tail coupling of styrene units but also head-to-tail styrene–styrene sequences.

EXPERIMENTAL

Materials

Polymerization-grade ethylene and extrapure nitrogen were purified further before feeding to the reactor by passing them through a DC-IB gas purification instrument. Toluene was refluxed over metallic sodium for 24 h and distilled under nitrogen atmosphere before use. Styrene was purified by distillation under reduced pressure over CaH$_2$, and was finally stored under nitrogen atmosphere. Cp*Ti(OBz)$_3$ and mMAO were prepared as described in the literature.[4,8] The contents of TMA retained in mMAO were determined by the pyridine titration method. Phenazine was used as the indicator and benzene as the solvent for the titration. Four types of mMAO solid, i.e., mMAO1, mMAO2, mMAO3, and mMAO4, con-

Table I   Copolymerization of Styrene with Ethylene and Successive Solvents Extractions of Product^a

Run No.	S/E in Feed mol/mol	Activity $\times 10^{-4}$ gP (mol Ti · h)$^{-1}$	S/E in Products mol/mol	M_w^b $\times 10^{-5}$	M_w/M_n	Wt % of Soluble Fraction in Boiling			St. mol % in Copolymers
						Butanone	THF	Residue	
1	100/0	36.7	100/0	6.8	2.3	1.5	0.5	98.0	—
2	0/100	7.4	0/100	5.6	2.1	trace	1.1	98.8	—
3	46/54	11.8	16/84	5.8	2.3	1.5	84.9	13.6	10.9
4	72/28	16.1	38/62	6.0	2.4	1.4	78.1	20.5	29.6
5	79/21	23.9	52/48	5.7	2.2	1.7	74.6	23.6	43.7
6	83/17	31.2	58/42	5.9	2.5	1.3	66.9	31.8	46.1

^{a} Polymerization conditions for all samples: [Ti] = 1.0×10^{-3} mol/L, [mMAO(TMA, 17.8 wt %)] = 0.2 mol/L, Al/Ti = 200, P(C$_2$H$_4$) = 0.13 Mpa, T_p = 60°C, t_p = 1 h, Toluene as solvent.
^{b} Calculated from the GPC curves.

Table II   Copolymerizations of Styrene with Ethylene using Cp*Ti(OBz)₃ Activated by Different mMAO

| Run No. | mMAO Sample | TMA in mMAO (wt %) | Ti Oxidation State (mol %) | | | Activity × 10⁻⁴ gP (mol Ti · h)⁻¹ | $M_w \times 10^{-5}$ | Boiling THF Soluble Fraction | | Boiling THF Insoluble Fraction | |
			Ti(II)	Ti(III)	Ti(IV)			Wt %	St. mol %	Wt %	St. mol %
5	mMAO1	17.8	0.6	19.3	80.1	23.9	5.7	74.6	43.7	23.6	98.7
7	mMAO2	20.8	4.3	58.5	37.2	25.7	5.4	32.9	66.3	65.4	100
8	mMAO3	23.6	8.8	66.7	24.5	30.4	5.2	18.8	87.5	80.6	100
9	mMAO4	25.9	12.3	73.6	14.1	41.8	4.5	10.6	98.6	89.2	100

Polymerization conditions: [Ti] = 1.0×10^{-3} mol/L, Al/Ti = 200, P(C₂H₄) = 0.13 MPa, [Styrene] = 6.49 mol/L, T_p = 60°C, t_p = 1 h. Toluene as solvent.

taining 17.8, 20.8, 23.6 and 25.9 wt % of TMA, respectively, were obtained.

Copolymerization

The polymerization runs were carried out in 150-mL glass flasks equipped with a magnetic stirrer under extrapure-grade nitrogen using the Schlenk line techniques. After mMAO, toluene, and styrene were introduced into the reactor, the reaction mixture was saturated with ethylene. Polymerization began following the injection of Cp*Ti(OBz)₃ and keeping a constant pressure of ethylene throughout the course of the polymerizations. The polymerizations were terminated by the addition of 10 wt % HCl in ethanol. The polymers were washed with ethanol and dried in vacuum to a constant weight at 80°C. The copolymerization products were extracted successively with boiling butanone and tetrahydrofuran (THF) in a Soxhlet extractor for 24 h.

Characterization

¹³C-NMR spectra were recorded at 80°C in *o*-dichlorobenzene using an INOVA500MHz spectrometer. Differential scanning calorimetry (DSC) analysis was conducted with a Perkin-Elmer DCS-7 system at 10°C/min. Gel-permeation chromatography (GPC) of polymers was performed on a Waters 150C using standard polystyrene as the reference and chloroform as the solvent at 40°C. A D/MAX-3AX diffractometer was used to obtain patterns by using a Ni-filtered Cu Kα X-ray beam.

RESULTS AND DISCUSSION

Copolymerization of Styrene with Ethylene

The results of copolymerization of styrene with ethylene under several monomer feeding ratios

Table III   Influences of Polymerization Temperature on Copolymerization of Styrene with Ethylene

| Run No. | T_p°C | Activity × 10⁻⁴ gP (molTi · h)⁻¹ | Composition of Copolymerization Products (wt %) | | | Composition of Copolymers (mol %) | |
			Copolymers	PE	PS	Styrene	Ethylene
10	0	2.8	trace	98.7	trace	—	—
11	20	7.2	trace	84.3	16.5	—	—
12	40	20.3	53.5	8.9	37.6	40.9	59.1
5	60	23.9	74.6	1.3	24.1	43.7	56.3
13	80	40.7	12.8	trace	86.3	58.3	41.7

Polymerization conditions: [Ti] = 1.0×10^{-3} mol/L, Al/Ti = 200, P(C₂H₄) = 0.13 Mpa, [Styrene] = 6.49 mol/L, t_p = 1 h, Toluene as solvent.

Table IV   Influence of Al/Ti Molar Ratio on Copolymerizations of Styrene with Ethylene Using Cp*Ti(OBz)$_3$ and mMAO1 Catalyst

Run No.	Al/Ti Ratio mol/mol	Activity × 10^{-4} gP (mol Ti · h)$^{-1}$	Composition of Products (wt %)			Composition of Copolymers (mol %)	
			Copolymers	PE	PS	Styrene	Ethylene
14	150	16.5	85.5	3.6	11.8	41.2	58.8
5	200	23.9	74.6	1.3	24.1	43.7	56.3
15	250	25.8	62.3	1.2	36.5	45.0	55.0
16	300	27.1	50.8	trace	49.2	44.1	55.9
17	400	31.9	29.8	trace	70.1	43.1	56.9

Polymerization conditions: [Ti] = 1.0 × 10^{-3} mol/L, P(C$_2$H$_4$) = 0.13 Mpa, [Styrene] = 6.49 mol/L, T_p = 60°C, t_p = 1 h, Toluene as solvent.

are summarized in Table I. Runs 3–6 were performed at increasing styrene concentrations and keeping ethylene at a constant pressure to change the monomer feed composition. To separate the copolymerization products, successive solvent extractions were carried out with boiling butanone and tetrahydrofuran (THF). It was found that boiling butanone-soluble fractions of homo- or copolymerization products were negligible (≤1.7%), and proved to be atactic polystyrene with ^{13}C-

NMR. Compared with both homopolymerization products of styrene and ethylene, the amounts of THF-soluble fractions of copolymerization products were much more. Accordingly, the THF-soluble fractions can be confirmed primarily to be copolymers, which will be further proven by structural characterization through ^{13}C-NMR in the following section. Increasing styrene concentration in the feed significantly increases both catalytic activity and styrene incorporation in the co-
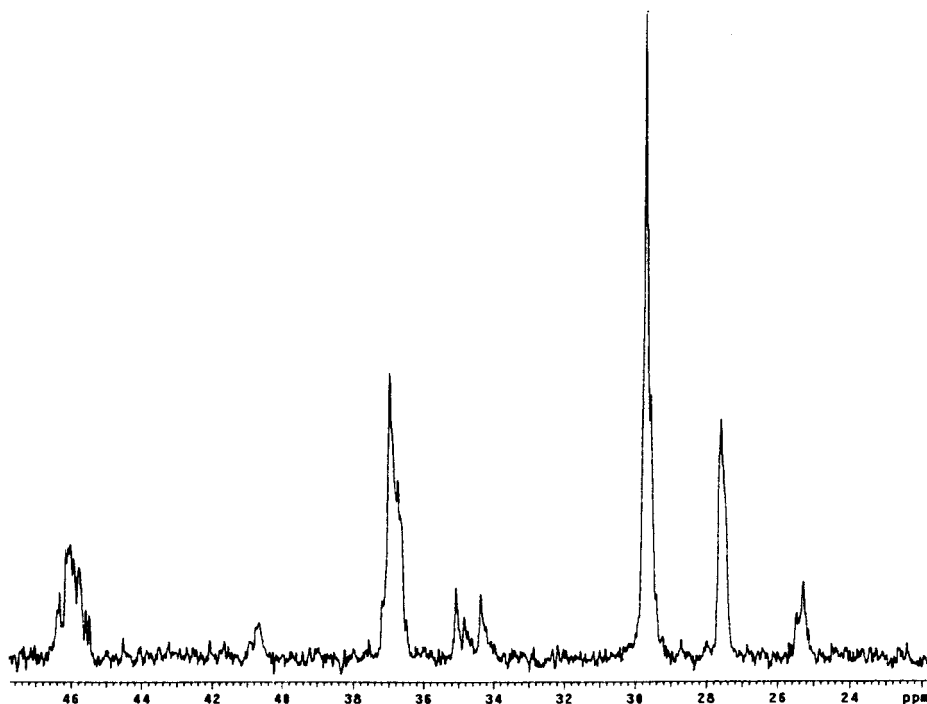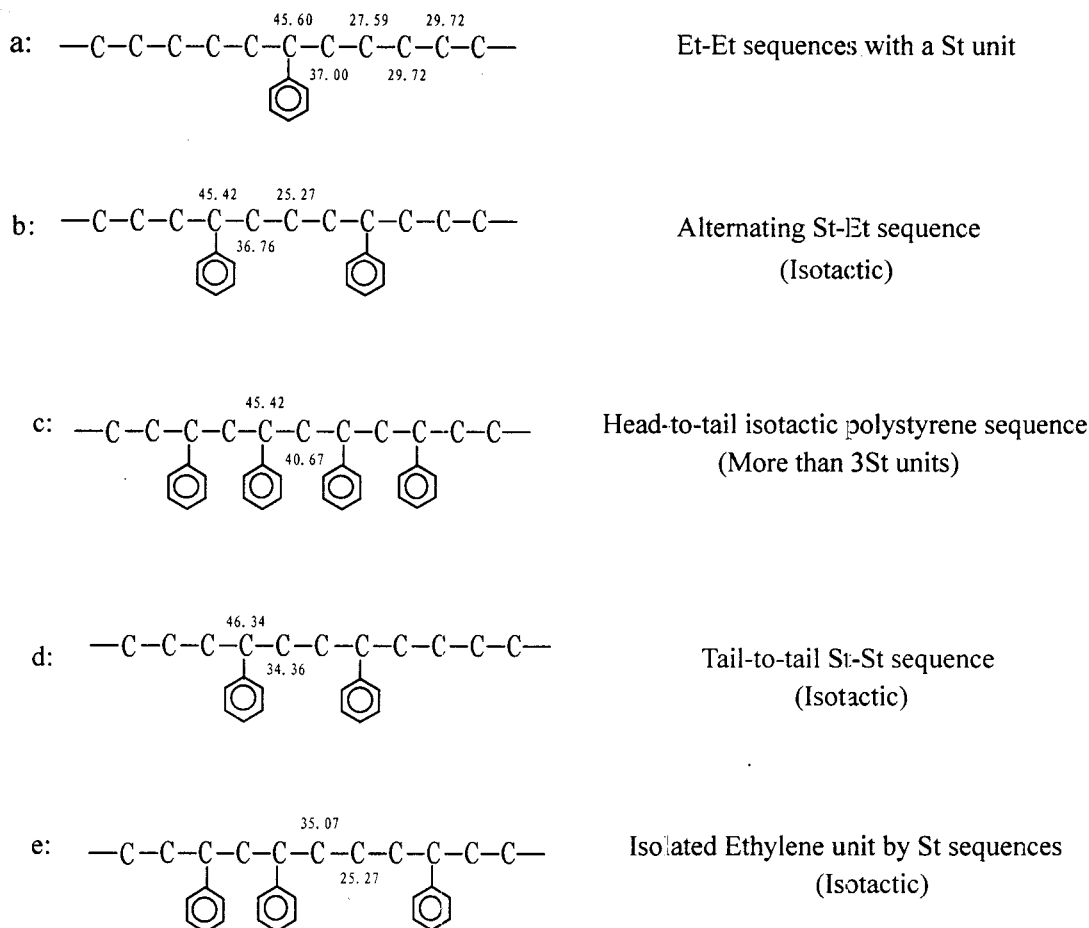

Figure 1 ^{13}C-NMR spectrum of THF-soluble fraction of a copolymerization product (run 5) prepared from the Cp*Ti(OBz)$_3$/mMAO1 catalyst.

a: —C—C—C—C—C—C—C—C—C—C—C—   Et-Et sequences with a St unit

b: —C—C—C—C—C—C—C—C—C—C—C—   Alternating St-Et sequence
(Isotactic)

c: —C—C—C—C—C—C—C—C—C—C—C—   Head-to-tail isotactic polystyrene sequence
(More than 3St units)

d: —C—C—C—C—C—C—C—C—C—C—C—   Tail-to-tail St-St sequence
(Isotactic)

e: —C—C—C—C—C—C—C—C—C—C—C—   Isolated Ethylene unit by St sequences
(Isotactic)

Scheme 1 Microstructure of poly(styrene-*co*-ethylene) obtained from THF soluble fractions of copolymerization products.

polymer, but the THF-soluble fraction of the copolymerization product is decreased.

MAO is the ubiquitous cocatalyst used in metallocene catalyzing olefin polymerization. It always contains some amount of unreacted TMA that cannot be removed easily by vacuum distillation. The residual TMA can be a factor influencing the catalytic activity of metallocene and molecular weight and structure of polyolefins and copolyolefins. The results of the copolymerization of styrene with ethylene, using Cp*Ti(OBz)$_3$ activated by four modified methylaluminoxanes (mMAO), are given in Table II. From run 7 to run 9, the higher the content of TMA in mMAO is, the more the Ti(IV) complexes are reduced to Ti(III) and Ti(II) states. The catalytic activity is increased with increasing content of Ti(III) active species. In run 9, the Ti(III) active species approaches 73.6 mol %, and the catalytic activity is

up to 41.8×10^4 gPS/mol Ti · h. TMA is not only a stronger reducing agent, but also a good chain transfer agent. Therefore, the excess TMA in mMAO, such as mMAO4, results in a decrease of molecular weight.

However, the THF-soluble fractions of copolymerization products, which are confirmed to be poly(styrene-*co*-ethylene), are increased with decreasing the content of TMA in mMAO. With these results, both active species may exit in the current system, where one [Ti(IV)] gives the copolymer of styrene and ethylene and the second [Ti(III)] only produces syndiotactic polystyrene (sPS).

The influences of temperature on copolymerization are shown in Table III. The catalytic activity and the content of styrene in the copolymerization products is increased with increasing the temperature. The content of ethylene in the copo-
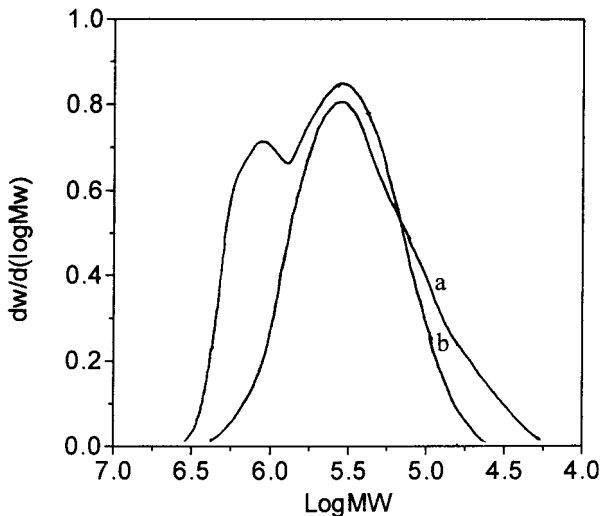
Figure 2 GPC curves of the polymers prepared from the Cp*Ti(OBz)$_3$/mMAO1 catalyst: (a) THF soluble fraction (run 5); (b) copolymerization product (run 5).

lymerization products becomes much more at temperatures below 60°C. This is because there are two active species in Cp*Ti(OBz)$_3$/mMAO catalyst systems, and a higher polymerization temperature is favorable to yield Ti(III) active species, which catalyze styrene syndiospecific polymerization, while more Ti(IV) active species promote ethylene polymerization at the lower temperature.

Table IV shows the results of copolymerizations of styrene with ethylene using the same concentration of Cp*Ti(OBz)$_3$ and different amounts of mMAO1 with 17.8 wt % TMA content. As mentioned above, TMA is a stronger reducing agent; therefore, the Ti(III) active species increase as the Al/Ti molar ratio is increased, and catalytic activity and the content of polystyrene in the copolymerization products is also increased. However, the composition of copolymers is not influenced by the Al/Ti molar ratio.

Characterization of Microstructure of Styrene and Ethylene Copolymers

To obtain purer copolymers of styrene and ethylene, the copolymerization products were fractionated by successive extraction with boiling butanone and teterahydrofuran (THF). As mentioned above, the butanone soluble fractions are atactic polystyrene. The THF-soluble and insoluble fractions were characterized by ^{13}C-NMR, GPC, and DSC.

All samples of THF-soluble fractions of copolymerization products analyzed by ^{13}C-NMR were very similar: the ^{13}C-NMR spectrum of THF-soluble fractions of run 5 in Table I is shown in Figure 1 as an example. Compared with both homopolymers, the presence of many new resonance peaks in the ^{13}C-NMR spectrum of the THF-soluble fraction implies that the fraction is a copolymer and its microstructure is very complicated. Scheme 1 depicts possible microstructures of the poly(styrene-*co*-ethylene) with 43.7 mol % styrene incorporation determined by elemental analyses.

Peaks observed at δ 27.58, 29.72, 37.00, and 45.60 ppm can be assigned to $S_{\beta\delta}$, $S_{\gamma\delta}(S_{\delta\delta})$, $S_{\alpha\delta}$, and $T_{\delta\delta}$ carbons of ethylene–ethylene sequences with a styrene unit (Scheme 1a), and δ 25.27, 36.76, and 45.42 ppm to $S_{\beta\beta}$, $S_{\alpha\gamma}$, and $T_{\delta\delta}$ carbons in alternating styrene–ethylene sequences (Scheme 1b). The resonances at δ 40.67 and 45.42 ppm correspond to the $S_{\beta\beta}$ and $T_{\beta\beta}$ carbons of isotactic polystyrene sequences, and more than β styrene units arranged head to tail (Scheme 1c). At the same time, the tail-to-tail isotactic polystyrene sequences are also found in the styrene–ethylene copolymer molecular chain, aiding the chemical shift of δ 34.36 and 46.34 ppm of $S_{\alpha\beta}$ and $T_{\gamma\delta}$ carbons (Scheme 1d). The resonances at δ 25.27 and 35.67 ppm are assigned to $S_{\alpha\gamma}$ and $S_{\beta\beta}$ in the isolated ethylene unit by styrene sequences (Scheme 1e).
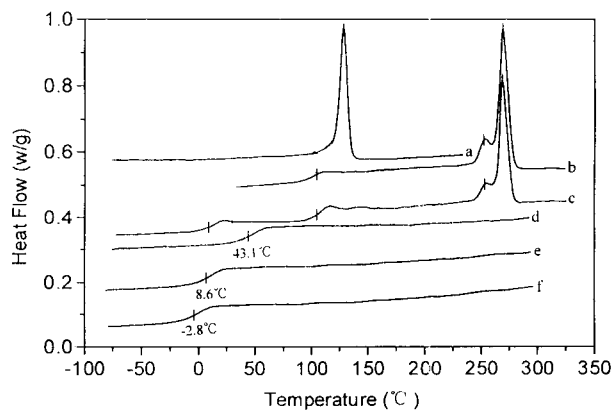

Figure 3 DSC diagram of sPS, PE, and poly(styrene-*co*-ethylene) obtained from the Cp*Ti(OBz)$_3$/mMAO1 catalyst: (a) PE from run 2; (b) sPS from run 1; (c) copolymerization product from run 5; (d) poly(styrene-*co*-ethylene) from run 15 (styrene = 45.0 mol %); (e) poly(styrene-*co*-ethylene) from run 5 (styrene = 43.7 mol %); (f) poly(styrene-*co*-ethylene) from run 12 (styrene = 40.9 mol %).
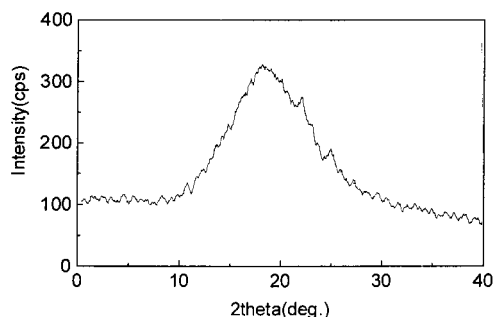
Figure 4   Wide-angle X-ray scattering curve of poly-(styrene-*co*-ethylene) from run 5.

The GPC curves of the THF-soluble fraction and copolymerization product of run 5 are shown in Figure 2. A unimodal shape and the narrow molecular weight distribution are observed in the GPC curve [Fig. 2(a)] of the THF-soluble fractions. This shows the characteristics of copolymerizations catalyzed by a single active species. However, the copolymerization product shows a bimodal shape [Fig. 2(b)], implying a corresponding blend of sPS, prepared by Ti(III) active species, and poly(styrene-*co*-ethylene) via Ti(IV) active species.

DSC measurements of the above copolymer of run 5 only show a single glass transition (T_g) at 8.6°C in Figure 3(e), which is different from that of sPS [Fig. 3(b)] and PE [Fig. 3(a)] homopolymers prepared using the same catalyst and in the same polymerization conditions. Apparently, although the copolymer has ethylene–ethylene and isotactic styrene–styrene sequences, it cannot crystallize. It is notable that the T_g is higher as styrene incorporation in the copolymer increases [Fig. 3(d)–(f)]. The wide-angle X-ray diffractogram for the polymer does not display a crystalline reflection in the 2θ 4−40° range (Fig. 4), supporting the DSC result.

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