Titanocene−Methylaluminoxane Catalysts for Copolymerization of Styrene and Ethylene: Synthesis and Characterization of Styrene−Ethylene Copolymers

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ABSTRACT: The copolymerization of styrene and ethylene has been performed using a titanocene-based catalytic system of cyclopentadienyltitanium triphenoxide ($CpTi(OPh)_3$) and methylaluminoxane (MAO). The catalyst system exhibited a high catalytic activity of 10^4−10^5 g (mof Ti·h)$^{-1}$ and was found to selectively (more than 90 wt %) give an elastoplastic and amorphous styrene−ethylene (S−E) copolymer with a well-defined random/alternating microstructure and a single glass transition (T_g) as thoroughly characterized by solvent fractionation, GPC, ^{13}C NMR, DSC, and WAXD. Under the reaction conditions employed, up to 54.5 mol % of styrene could be introduced into the copolymer chains. The composition, microstructure, molecular weight of the copolymers, and catalytic activity of the copolymerization are strongly dependent upon the comonomer feed ratio, polymerization temperature (T_p), $CpTi(OPh)_3$/MAO mole ratio, and trimethylaluminum (TMA) content or structure in MAO. For $300 \leqslant Al/Ti < 1000$, the copolymerization product was essentially the random S−E copolymer. For $1000 < Al/Ti \leqslant 2000$, the copolymerization product was significantly SPS homopolymer. The results showed that 24.5−28.2 mol % TMA content in MAO (oligomerization degree (n) ≈ 18−20) was optimum for the copolymerization, but 30.2−35.7 mol % TMA in MAO (oligomerization degree (n) ≈ 24−28) for styrene syndiospecific homopolymerization, even in the presence of ethylene feed monomer. The external addition of TMA or triisobutylaluminum (TIBA) inhibited the copolymerization but promoted the styrene homopolymerization. ESR spectroscopic analysis combined with copolymerization results suggests the presence of a Ti(IV) active center which is responsible for the formation of polyethylene, a Ti(III) species which is active in the syndiospecific polymerization of styrene, and, moreover, the presence of a third intermediate which contributes to promoting the copolymerization of styrene with ethylene to produce S−E copolymer.

Introduction

Great interest has been devoted to the synthesis of well-defined styrene/α-olefin copolymers with new microstructure by stereospecific control. These new copolymers are expected to have unique mechanical performance, but no new technologies regarding processing, stabilization, disposal, recycling, etc. need to be developed. In the past decade much effort has been expended in fulfilling the copolymerization of styrene and α-olefins with heterogeneous Ziegler−Natta catalysts.[1] However, many technical problems remain unresolved. In most cases, claims of styrene/α-olefin copolymer formation with Ziegler−Natta catalytic systems have not been proven directly but instead inferred from physical properties and the method of synthesis. Experimental evidence has shown that many of these commercial claims are indeed nothing more than intimate blends of homopolymers which show enhanced properties due to the fine level of dispersion achieved by in situ polymerization.[2]

The discovery of homogeneous group 4 metallocene−methylaluminoxane catalysts that combine high activity with excellent stereoregularity in the stereospecific polymerization of α-olefins or styrene has led to a resurgence of interest in this field.[3] It is believed that metallocene catalytic systems will open up the possibility of controlling stereospecificity in styrene or olefin polymerization/copolymerization at the molecular level and making use of it to produce polymers with new microstructure.[2b,4] This can be attributed to the following factors: first, to the versatility of these catalysts in controlling the tacticity (e.g. isotactic, stereoblock, syndiotactic) and the performance (including narrow molecular weight distribution, well-defined microstructure and near-uniform composition) of polymers formed by changing the structural characteristics of the ligand;[5] second, to the universality of these catalysts in promoting isospecific or syndiospecific polymerization of not only α-olefins but also cyclic olefins, polar vinyl monomers, vinyl aromatics, and dienes;[6] third, to the increased activity and the true "single-site" formation of the metallocene catalysts[7] compared with traditional Ziegler−Natta catalysts. Therefore, it occurred to us that metallocene catalysts, designed by changing the structure of ligands, can be expected to produce true styrene/α-olefin copolymers with a new well-defined microstructure.

Until recently, only several homogeneous catalyst systems based on zirconocene or titanocene and methylaluminoxane (MAO) have been used to copolymerize styrene with ethylene and, depending on the polymerization conditions and the catalyst performance, produce alternating, block, and pseudorandom styrene−ethylene copolymers.[8−17] Kakugo and his co-workers[8] first reported the synthesis of a crystalline alternating styrene−ethylene copolymer, showing isotactic styrene units and a melting point of 116 °C, by using a catalyst composed of [2,2′-thiobis(4-methyl-6-*tert*-butylphenoxy)]titanium dichloride and MAO. Later on, a new type of styrene−ethylene diblock copolymer with syndiotactic styrene units became available based on a titanocene catalyst, such as (pentamethylcyclopentadienyl)titanium trimethoxide/MAO.[9] More recently, a similar styrene−ethylene block copolymer was also obtained by using (cyclopentadienyl)[bis(trimethylsilyl)amido]titanium

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dichloride and MAO.[10] Stevens et al.[11] reported the copolymerization of styrene and ethylene promoted by bridged amidomonocyclopentadienyl Ti or Zr complexes, for example, [(phenylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silane]titanium dichloride and MAO. The copolymers obtained were called "pseudorandom", due to no regioregularly arranged −SS− sequences in the ^{13}C NMR. Analogous copolymers have been synthesized by using metallocene-based catalytic systems such as cyclopentadienyltitanium trichloride ($CpTiCl_3$)−MAO,[12] (hexamethyltrisiloxanediyl)bis(cyclopentadienyltitanium trichloride)−MAO,[13] [isopropylidene(1-cyclopentadienyl)(9-fluorenyl)]zirconium dichloride−MAO,[14] [(methyl)(phenyl)methylene(1-cyclopentadienyl)(9-fluorenyl)]zirconium dichloride−MAO,[15] [(*tert*-butylamino)-dimethyl(tetramethyl-η^5-cyclopentadienyl)silane]titanium dichloride−MAO,[16] and η^5-$C_5Me_5Ti(CH_2Ph)_3$−B-$(C_6F_5)_3$.[17]

As compared with zirconium-based catalysts, titanium-based catalysts indeed show reasonable catalytic activity and enhanced monomer incorporation for copolymerization of styrene with ethylene. However, previous studies still leave much to be desired due to very low catalytic activity, low level of monomer incorporation, and lack of demonstrated evidence of regioselectivity of insertion, especially at higher levels of monomer incorporation. On the other hand, inconsistent results on copolymerization of styrene with ethylene by using titanocene-based catalysts have caused much controversy. The point in controversy is whether titanocene-based catalysts can produce styrene−ethylene copolymer or give intimate blends of homopolymers. More recently, Seppala and Aaltonen[18,19] reported, in contrast to an earlier study,[12] that a titanocene-based catalyst of $CpTiCl_3$ and MAO did not give a true styrene−ethylene copolymer but a mixture of syndiotactic polystyrene (SPS) and polyethylene. A similar conclusion was made in other titanium-based catalyst systems, such as trichloro(2,6-di-*tert*-butylphenoxy)titanium and MAO.[20] In this paper, we report our results on the synthesis and characterization of styrene−ethylene copolymers obtained by using a titanocene-based catalyst of cyclopentadienyltitanium triphenoxide [$CpTi(OPh)_3$] and methylaluminoxane (MAO). Although $CpTi(OPh)_3$ was reported as a catalyst to catalyze styrene polymerization using MAO as cocatalyst,[21] its utility as a catalyst to catalyze the copolymerization of styrene with ethylene is reported for the first time.

Experimental Section

Materials. Polymerization-grade ethylene and extra-pure-grade nitrogen were further purified before feeding to the reactor by passing them through a DC-IB gas purification instrument.

Toluene was refluxed over metallic sodium/benzophenone for 48 h and distilled under a nitrogen atmosphere before use. Styrene was purified by distillation under reduced pressure over CaH_2. $CpTi(OPh)_3$ was prepared as described in the literature[22] and stored in a glovebox under extra-pure-grade nitrogen.

Methylaluminoxane (MAO) was prepared as follows: Finely pulverized $Al_2(SO_4)_3{\cdot}18H_2O$ (62.0 g) dispersed in 120 mL of toluene was cooled at −10 °C in a 500 mL flask equipped with a magnetic stirrer, a nitrogen inlet, and a syringe pump to control the addition rate of trimethylaluminum (TMA) solution. TMA solution (3.0 M, 200 mL) was added dropwise over 1 h. The mixture was warmed slowly to room temperature and stirred for several hours. The temperature of the reaction mixture was slowly raised to 60 °C, and the reaction was allowed to continue for 24 h. The product was separated by filtration. The filtrate was concentrated under reduced pressure by process-controlling the temperature from 20 to 80 °C. The white colored glassy MAO (in 40% yield) was stored in a glovebox and weighed when required.

Copolymerization. The copolymerizations were performed at a constant ethylene pressure of 860 mmHg in a 100 mL glass flask provided with a magnetic stirrer and thermostated at 60 °C in an oil bath. The reactor was charged under nitrogen sequentially with toluene (30 mL), styrene (10 mL), and a prescribed amount of MAO; the inert gas was removed, and then the reactor was saturated with ethylene. A prescribed amount of metallocene, activated with MAO in toluene 10 min in advance, was injected into the reactor by a syringe, and then copolymerization was started. The flask was continuously fed with ethylene to keep monomer concentration constant. The copolymerization was terminated after 1 h by the addition of a 5% solution of HCl in methanol. The copolymerization products were washed with fresh methanol and dried in vacuo.

Solvent Extraction. Selective solvent fractionation to remove homopolymers was carried out using a Soxhlet extractor. Approximately 10 g of copolymerization product was placed in a cellulose thimble and extracted successively with boiling methyl ethyl ketone (MEK) for 12 h to remove the soluble atactic polystyrene and then with boiling tetrahydrofuran (THF) for another 28 h to remove the insoluble SPS and PE homopolymers. The THF-soluble extracts were isolated by evaporation of the solvent, dried under vacuum, weighed, and analyzed by GPC, DSC, and ^{13}C NMR spectroscopy.

Characterization. Gel permeation chromatography analysis was conducted on a Waters 150C high-temperature gel permeation chromatograph using standard polystyrenes as reference and 1,2,4-trichlorobenzene as eluent at 135 °C. ^{13}C NMR spectra were recorded at 130 °C in *o*-dichlorobenzene using a JEOL FX-100 spectrometer. The glass transition temperature and melting temperature were determined with a Perkin-Elmer DSC-2 system at 10 °C/min. Any thermal history difference in the polymers was eliminated by first heating the specimen to above 280 °C, cooling at 10 °C/min to −100 °C, and then recording the second DSC scan. Wide-angle X-ray diffraction measurements were made using a Ricon D/Max-3A diffraction system. The radiation source was nickel-filtered Cu Kα (35 kV and 25 mA). The samples were scanned over a 2θ range of 5−40° at a scan rate of 0.02°/s. Membrane samples were annealed in a vacuum oven at 80 °C for 1 h and allowed to cool slowly prior to analysis.

Electron spin resonance (ESR, Bruker ECS-106) was used and quantitative determination of the amount of ESR-observable Ti^{3+} was carried out by double integration of the ESR spectrum as described by Chien et al.[23]

Results and Discussion

Synthesis of Styrene−Ethylene Copolymer. Copolymerization of styrene (S) with ethylene (E) was conducted under variable monomer feeding ratios in the presence of the $CpTi(OPh)_3$/MAO catalytic system (Table 1). The details of the polymerizations are reported in the Experimental Section.

To determine homopolymer and/or copolymer in the copolymerization products, selective solvent fractionation was carried out successively with boiling MEK and THF solvents. It was found that MEK was a good solvent for atactic polystyrene and that THF was a poor solvent for syndiotactic PS and PE homopolymer but good for styrene−ethylene (S−E) copolymers. The amounts of MEK-soluble fractions are negligible ($\leqslant$1%), but the amounts of MEK-insoluble fractions are over 99%, indicating the absence of atactic polystyrene. As compared to the MEK-soluble fraction, the amounts of THF-soluble fractions are significant and reach as high as 90%, but THF-insoluble fraction is as low as 10% in runs 2−6 of Table 1. From Figure 1 it can be seen that the MWD curve of the THF-soluble fractions shows a

Table 1. Copolymerization of Styrene (S) and Ethylene (E) with the CpTi(OPh)$_3$/MAO Catalytic System[a]

			THF-soluble fraction						THF-insoluble fraction				
run	S/E in feed (mol/mol)	activity[b] $\times 10^{-5}$	yield[c] (%)	M_w[d] $\times 10^{-4}$	M_w/M_n	styrene[e] incorporation (mol %)	T_g[f] (°C)	T_m[f] (°C)	yield[g] (%)	M_w $\times 10^{-4}$	M_w/M_n	T_g (°C)	T_m (°C)
1	100/0	16.00[h]	1.0	0.8	2.7		99.7	258.2	99.0	12.0	2.5	99.7	260.5
2	80/20	1.46	92.2	8.2	3.3	54.5 (45.5)[i]	35.5	nd[j]	7.8	6.2	bimodal	−68.0, 99.8	129.8, 258.5
3	70/30	1.12	90.2	6.5	3.2	44.1 (55.9)[i]	28.2	nd[j]	9.8	4.0	bimodal	−67.0, 99.7	127.1, 258.2
4	50/50	0.96	91.3	3.9	3.4	29.7 (70.3)[i]	23.5	nd[j]	8.7	4.1	bimodal	−68.0, 98.5	128.0, 257.2
5	40/60	0.85	91.9	2.5	3.2	23.3 (78.7)[i]	18.2	nd[j]	8.1	3.5	bimodal	−68.0, 99.1	127.8, 253.5
6	28/72	0.63	90.8	2.7	3.4	18.5 (81.5)[i]	15.8	nd[j]	9.2	3.4	bimodal	−67.5, 98.7	127.4, 255.1
7	0/100	0.80	0.8	0.7	2.3		−68.0	130.5	99.2	6.7	2.0	−68.0	130.5

[a] Polymerization conditions: T_p 60 °C; t_p, 1 h; CpTi(OPh)$_3$, 0.2 mM; MAO (TMA, 26.5 mol %), 0.118 M; Al/Ti (mol/mol), 589; total volume (toluene + styrene), 40 mL; ethylene pressure, 860 mmHg. [b] Activity in units of g of polymer/(mol of Ti·h). [c] Weight percent of THF-soluble fraction. [d] Calculated fromthe GPC curve. [e] Calculated from ^{13}C NMR. [f] Determined by DSC. [g] Weight percent of THF-insoluble fraction. [h] t_p, 1 h; CpTi(OPh)$_3$, 0.11 mM; Al/Ti (mol/mol), 1000; styrene, 1.75 M; toluene, 30 mL; syndiotactic index 99%. [i] The data in the paratheses denote the ethylene content in the copolymer. [j] Not detected.

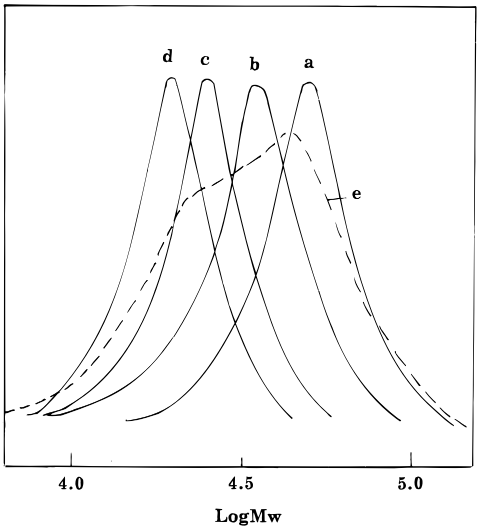

Figure 1. Molecular weight (M_w) distribution curves of the polymers prepared from CpTi(OPh)$_3$/MAO catalyst: (a) syndiotactic polystyrene (SPS) (syndiotactic index ≥ 98%); (b) THF-soluble fraction (run 2); (c) THF-soluble fraction (run 4); (d) THF-soluble fraction (run 6); (e) THF-insoluble fraction (run 2).

unimodal shape, while that of the THF-insoluble fractions shows a bimodal shape similar to that of corresponding SPS/PE blend. The THF-soluble fraction shows a single glass transition (T_g) between the glass transitions of PS and PE homopolymers but without a melting transition (Table 1). In contrast, the THF-insoluble fraction shows two melting transitions (T_m) and two distinct glass transitions (T_g) which coincide with the respective T_m's and T_g's of PE and SPS homopolymers. On the other hand, control fractionation experiments show that SPS and PE homopolymers, obtained under identical polymerization conditions with that of runs 2−6 in Table 1, are almost insoluble in THF, and the amounts of THF-soluble fraction are less than 1%, which results from low molecular weight fractions. Therefore, these results indicate that the THF-soluble fraction of copolymerization product is a S−E copolymer without contamination of homopolymers or homopolymer mixtures, while the THF-insoluble fractions are a blend of SPS and PE homopolymers.

As seen from Table 1, CpTi(OPh)$_3$/MAO catalyst shows a high activity of 1.6×10^6 g of PS/((mol of Ti)·h) and excellent syndiotacticity (⩾99%) for syndiospecific polymerization of styrene, in agreement with the result reported by Chien.[21] At the same time, the catalyst also shows a reasonable catalytic activity of 8.0×10^4 g of PE/((mol of Ti)·h) for ethylene polymerization at a constant ethylene pressure of 860 mmHg although it has a lower activity than has been reported for the zirconocene catalysts, presumably due to the relative ease of change of oxidation number in the Ti active species.[24] As to the copolymerization of styrene with ethylene, it was found that the CpTi(OPh)$_3$/MAO catalytic system had a high catalytic activity compared with CpTiCl$_3$/MAO[12] and a zirconocene catalyst.[14,15] Increasing the ethylene concentration in the feed clearly decreases the catalytic activity but increases the ethylene incorporation in the copolymer, while increasing styrene concentration in the feed significantly increases both the catalytic activity of copolymerization and styrene incorporation in the copolymer. By adjusting the feed ratios, copolymers containing as high as 54.5 mol % styrene could be synthesized. The content of the S−E copolymers is never less than 90% by weight in total copolymerization products, no matter what the S/E ratio of the feed is. Besides the S−E copolymer, the copolymerization products contain a small amount of syndiotactic polystyrene and polyethylene, suggesting that the active species producing S−E copolymer is different from that producing SPS and PE homopolymers. This will be further supported by structural identification through ^{13}C NMR in the next section.

As compared to styrene homopolymerization, the addition of ethylene lowers the M_w and broadens the molecular weight distribution (MWD) of the copolymer (Table 1). The M_w of the copolymer decreases with an increase of ethylene concentration in the feed. A likely explanation for the decrease in M_w of the copolymer is the greater probability of chain transfer as the copolymer concentration increases, presumably due to the relatively weak coordination or electron-donating property of ethylene in the catalyst system studied as compared with styrene. The difference in the polydispersities between homopolymers and the copolymer may suggest that these polymerizations proceed over different active species, in consonance with results obtained in solvent extraction fractions.

Table 2 shows the effect of polymerization temperature (T_p) on catalytic activity, the incorporation of styrene in copolymer, and the molecular weight of the copolymer. It was found that the composition of the copolymerization products was strongly dependent on the polymerization temperature. Little, if any, S−E copolymer was obtained at T_p < 30 °C; significant amounts of copolymer, although mixed with polyethylene (PE) and syndiotactic polystyrene (SPS) homopolymers, were obtained at T_p ⩾ 40 °C. This suggests that the active species promoting the copolymerization results from a reaction requiring a higher temperature.

Table 2. Copolymerization of Styrene (S) and Ethylene (E) at Different Polymerization Temperatures[a]

run	S/E in feed (mol/mol)	temp (°C)	activity[b] × 10^{-5}	comp of copolym products (wt %)			S–E copolymer[e]	
				S–E[c]	PE[d]	SPS[d]	M_w	styrene[f] (mol %)
8	80/20	0[g]	0.05	trace	≥92	≤8		
9	80/20	30	0.12	15.7	70.2	14.1	12.3	21.2
10	80/20	40	0.93	62.1	20.5	17.4	10.5	38.4
11	80/20	60	1.46	92.2	2.4	5.4	8.2	54.5
12	80/20	80	0.90	30.0	6.0	64.0	5.8	65.1
13	50/50	0[g]	0.03	trace	≥95	≤5		
14	50/50	30	0.08	18.5	71.5	10.0	8.9	9.8
15	50/50	40	0.42	59.2	30.3	10.5	6.2	12.5
16	50/50	60	0.96	91.8	6.0	2.2	4.2	29.8
17	50/50	80	0.34	28.3	10.0	61.7	3.0	40.1

[a] Polymerization conditions: see Table 1. [b] Activity in units of g of polymer/(mol of Ti)·h). [c] Calculated fromthe THF-soluble fraction. [d] Estimated from elemental analysis and ^{13}C NMR spectra of the THF-insoluble fraction. [e] THF-soluble fraction. [f] Estimated from the ^{13}C NMR spectra of the THF-soluble fraction. [g] Polymerization time, 3 h.

However, the amount of S–E copolymer, together with copolymerization activity, has a maximum value at 60 °C, below or above which catalytic activity decreases. The amount of PE homopolymer increases with decreasing temperature and becomes more and more significant at temperatures below 40 °C, while the amount of SPS homopolymer becomes favored at temperatures above 60 °C in the copolymerization. The variation of the composition of copolymerization products with the T_p indicates that temperature may affect the formation and type of active site. As a matter of fact, electron spin resonance (ESR) analysis of MAO-activated $CpTi(OPh)_3$ catalyst in the presence of comonomers shows that, with increasing polymerization temperature, the resonances centered at $g = 1.977$ are slowly split into a complex signal and thereafter are replaced by a strong ESR signal showing two components at $g = 1.974$ and $g = 1.968$, suggesting that partial or significant reduction of Ti(IV) to Ti(III) occurs during the copolymerization. This result provides very strong evidence that the active species for the formation of PE, SPS, and S–E copolymer are quite different.

It is notable that the composition of S–E copolymer seems, at a constant polymerization temperature, to be independent of the feed composition. Incorporation of styrene in the copolymer, however, increases with increasing polymerization temperature. According to the Arrhenius equation, the Arrhenius plot gave $\Delta E_p \approx 0$ kcal/mol for ethylene polymerization but $\Delta E_p = 7.6$ kcal/mol for styrene polymerization. Therefore, the fact that higher temperature favors higher styrene incorporation in the copolymer may be attributed to higher activation energies (ΔE_p) for migratory insertion and propagation of styrene than ethylene. Of course, there are probably other factors which arise from the high polymerization temperature and the formation of Ti(III) species promoting styrene polymerization (vide infra). This dependence of the styrene incorporation in the copolymer produced on T_p, especially at high T_p, is similar to the behavior observed during isotactic-specific copolymerization of styrene with ethylene[25] and styrene with propene[26] by using heterogeneous $MgCl_2$-supported $TiCl_4/NdCl_3/AlR_3$ catalyst.

Table 3 presents the results of styrene–ethylene copolymerization using the same [Ti] but different amounts of MAO with 26.5 mol % TMA content. As can be seen, there is a critical amount of MAO below which there is no polymerization. It is well-known in homogeneous metallocene catalyst systems that catalytic activity is strongly influenced by the Al/Ti molar ratio employed. From the solvent fractionation studies, it can be seen that the yield of copolymer obtained decreases while homopolymer content increases as the Al/Ti molar ratio is increased. The styrene incorporation in the copolymer increases with an increase of Al/Ti molar ratio up to 1500 and thereafter almost remains constant. For Al/Ti < 400, the copolymerization by $CpTi(OPh)_3$/MAO produced both a THF-soluble fraction, which was S–E copolymer with a single glass transition (T_g) and a unimodal GPC curve, and a THF-insoluble fraction, which was polyethylene (PE) homopolymer with $T_g = -68$ °C and $T_m = 130.5$ °C identical to that of PE obtained by homopolymerization. Styrene homopolymerization did not occur at Al/Ti < 400, probably because the catalytic activity of styrene syndiospecific polymerization is very sensitive to [MAO].[27] For $400 \leqslant$ Al/Ti $\leqslant 1500$, the copolymerization not only produced S–E copolymer and PE homopolymer but also produced syndiotactic polystyrene (SPS) homopolymer. SPS homopolymer increased whereas both PE homopolymer and S–E copolymer decreased with increasing Al/Ti molar ratio. For Al/Ti $\geqslant 2000$, however, the copolymerization produced a negligible THF-soluble fraction but essentially THF-insoluble fraction; the insoluble fractions were almost SPS homopolymer. These findings suggest that there are at least two or may be even more active species depending upon the Al/Ti molar ratio.

The molecular weights (M_w) of the S–E copolymer decrease while the molecular weight distributions increase with increasing Al/Ti molar ratio, probably attributable to the enhancement of chain transfer to MAO or TMA in MAO during the chain propagation.

To understand the nature of the active species in the copolymerization, we investigated the variation of oxidation states of titanium in a $CpTi(OPh)_3$/MAO mixture as a function of [MAO] by the ESR method described by Chien et al.[23] The results showed that the percentage of Ti(III) was 35.5–55.2 at Al/Ti = 400–800 but 75.3–95.7 at Al/Ti = 1500–2000. The higher the Ti(III) content, the lower the copolymer yield as combined with results in Table 3. A higher Al/Ti molar ratio contributes to reduction of Ti(IV) to Ti(III) active complex, and the latter may actually be the active species in styrne syndiotactic polymerization to give syndiotactic polystyrene.[27,28] Chien et al.[3i] have studied the catalyst structure of $CpTi(OBu)_3$/MAO catalyst for styrene polymerization. ESR spectroscopic data combined with redox titration analysis suggest that a Ti(III) complex or a neutral hybride [Ti(III)–H] complex is the active species in the styrene syndiospecific polymerization. More recently, Grassi et al.[29a] found that the $Cp^*Ti(CH_2C_6H_5)_3/B(C_6F_5)_3$ catalyst produced a mixture of a cationic Ti(IV) complex, $[Cp^*Ti(CH_2C_6H_5)_2]^+[B(CH_2C_6H_5)(C_6F_5)_3]^-$, and Ti(III) complexes, possibly $[Cp^*Ti(CH_2C_6H_5)]^+[B(CH_2C_6H_5)(C_6F_5)_3]^-$, as characterized by NMR and electron spin resonance (ESR) spectroscopy in the styrene syndiospecific polymerization. It has been suggested, on the basis of kinetic homopolymerization results,[29b] that the former complex is only able to promote the polymerization of ethylene, while the latter is active in the syndiospecific polymerization of styrene. A similar conclusion was also made in the $Cp^*Ti(CH_3)_3/B(C_6F_5)_3$ catalytic system for styrene polymerization.[29c] The cationic Ti(IV) complex $Cp^*Ti(CH_3)_2^+$, produced in the reaction of $Cp^*Ti(CH_3)_3$ and

Table 3. Effect of the MAO/Ti Molar Ratio on the Copolymerization of Styrene and Ethylene with the $CpTi(OPh)_3$/MAO Catalytic System[a]

			THF-soluble fraction						THF-insoluble fraction					
run	Al/Ti (mol/mol)	activity[b] × 10^{-5}	yield[c] (wt %)	M_w[d] × 10^{-4}	M_w/M_n	styrene[e] incorp (mol %)	T_g[f] (°C)	T_m[f] (°C)	yield[g] (wt %)	M_w[d] × 10^{-4}	M_w/M_n	T_g (°C)[f]	T_m (°C)[f]	sytrene[h] content (wt %)
18	200	0												
19	300	0.15	98.5	9.8	3.4	27.5	21.0	nd[i]	1.5	7.8	3.2	−68	131.0	nd[i]
20	400	0.67	95.8	6.5	3.2	28.0	21.5	nd[i]	4.2	7.2	3.8	−68, 100 (weak)	130.8, 257.5 (weak)	8.2
21	600	1.00	91.8	3.8	3.4	29.5	22.9	nd[i]	8.2	8.5	bimodal	−68, 98.8	129.8, 258.2	23.7
22	800	1.25	90.5	2.5	3.5	31.2	23.2	nd[i]	9.5	9.8	bimodal	−67, 99.5	127.5, 257.6	45.9
23	1000	1.88	56.0	2.3	3.7	43.9	23.5	nd[i]	44.0	10.2	bimodal	−68, 99.2	128.4, 258.1	70.4
24	1500	2.50	15.3	2.0	4.2	44.5	24.0	nd[i]	80.7	9.1	bimodal	−68 (weak) 99.8	128.4 (weak) 259.8	94.8
25	2000	2.70	2.5	2.0	4.5	44.7	25.5	nd[i]	97.5	7.5	2.8	99.7	260.1	98.5

[a] Polymerization conditions: S/E in feed, 50/50; other conditions, see Table 1; internal TMA content in MAO, 26.5 mol %. [b] Activity in units of g of polymer/(mol of Ti)·h). [c] Weight percent of THF-soluble fraction. [d] Calculated from GPC curve. [e] Calculated from ^{13}C NMR. [f] Determined by DSC. [g] Weight percent of THF-insoluble fraction. [h] Estimated from elemental analysis and ^{13}C NMR spectra of the THF-insolbule fraction. [i] Not detected.

Table 4. Effect of TMA in MAO on the Copolymerization of Styrene and Ethylene with the $CpTi(OPh)_3$/MAO Catalytic System[a]

			comp of copolym products (wt %)		
run	TMA in MAO[b]	activity[c] × 10^{-5}	copolymer[d]	SPS[e]	PE[e]
26	5.5	0	0	0	0
27	10.2	0.08	0	29.2	70.8
28	15.8	0.23	2.8	38.5	58.7
29	21.5	0.63	50.2	15.5	34.3
30	24.5	1.25	90.5	5.0	4.5
31	26.5	1.24	86.5	6.8	6.7
32	28.2	1.33	80.3	12.5	7.2
33	30.2	1.84	10.2	75.3	14.5
34	35.7	1.69	5.1	88.3	6.6
35	37.5	0.93	5.8	87.8	6.4

[a] Polymerization conditions: MAO, 0.16 M; Al/Ti (mol/mol), 800; S/Ein feed, 50/50 (mol/mol); other conditions, see Table 1. [b] Activity in units of g of polymer/((mol of Ti)·h). [c] TMA content was determined from the NMR spectrum; oligomerization degree (*n*) of MAO, 18. [d] Calculated from the THF-soluble fraction. [e] Estimated from elemental analysis and ^{13}C NMR spectra of the THF-insolbule fraction.

$B(C_6F_5)_3$, slowly and partially decomposes to the cationic Ti(III) complex $Cp^*Ti(CH_3)^+$, which promotes the syndiotactic polymerization of styrene. Therefore, it is believed that in the $CpTi(OPh)_3$/MAO catalytic system studied, one type of active species may be a cationic titanium Ti(IV) complex which contributes to PE homopolymer, a second may be a Ti(III) or a neutral hydride [Ti(III)−H] complex which essentially produces SPS homopolymer, and a third possibility is an intermediate complex which is responsible for the S−E copolymerization. Further studies are under way on the structural characterization of active species in the copolymerization of styrene with ethylene.

As mentioned in Tables 2 and 3, the formation of the active species not only depends upon the polymerization temperature but also relies on the MAO/Ti mole ratio. Therefore, the sources and composition of MAO may play a great role in the formation of the active species, thus strongly controlling the catalytic activity and the composition of the copolymerization product. It is well-known that there is always a small, but definite amount of TMA present along with MAO,[30] depending upon the conditions of the hydrolysis of TMA and the thermal treatment of the hydrolysis products. A very different effect was observed when the same [Ti] but different sources of MAO were used. As can be seen in Table 4, the MAO containing lower concentration of TMA (as low as 5 mol %) shows no effectiveness in activating $CpTi(OPh)_3$ for promoting the syndiospecific homopolymerization and copolymerization of styrene and/or ethylene. Thereafter, the catalytic activity increases in both the copolymerization and homopolymerization with increasing amount of TMA in MAO. At low TMA concentration (as low as 10 mol %), the copolymerization product is a mixture of homopolymers, mainly polyethylene, with no detectable amount of copolymer. When the concentration of TMA in MAO increases, the copolymerization product is mainly copolymer but further increase in TMA results in the formation of almost pure syndiotactic polystyrene. Accordingly, ESR analysis of different MAO-activated catalytic systems does show that during the S−E copolymerization partial or almost total reduction of Ti(IV) to Ti(III) occurs with increasing TMA concentration in MAO. This is attributable to the stronger alkylating and reducing performance of TMA in MAO. Consequently, the results discussed here further support this hypothesis and suggest that there are three types of active species which are responsible for the formation of PE, SPS, and S−E copolymer, respectively (vide supra).

As mentioned above, MAO must contain a critical amount of TMA, depending upon the properties of the monomer and catalyst system, to activate the metallocene catalyst to form the active species for the homopolymerization or copolymerization. The results show that 24.5−28.2 mol % TMA in MAO is optimum to get a high catalytic activity for the styrene−ethylene copolymerization, but 30.2−35.7 mol % TMA in MAO for the styrene syndiospecific polymerization. Apart from contributing to the formation of active species and increasing the catalyst activity, an optimum amount of TMA may also play the more important role of stabilizing the active species and extending the catalyst lifetime, probably by suppressing the side reactions shown by Kaminsky et al.[6d]

In addition, it is interesting to note that the MAO, obtained by changing the hydrolysis conditions (water/Al mole ratio, thermal treatment, etc.), showed different cocatalyzing performance in copolymerization even if containing identical TMA concentration in MAO. Whereas a particular MAO could activate $CpTi(OPh)_3$ to promote homopolymerization of styrene or ethylene, some others essentially promote the copolymerization. These findings suggest that the presence of TMA, either "free" or "complex", is not the only important factor influencing the copolymerization. A likely explanation for the differences in performance among the various kinds of MAO is based on its composition and structural characteristics (e.g. linear, cyclic, ladder, associated aggregates, even analogous three-dimensional cages with different coordinative aluminum centers as de-

Table 5. Effect of the External Addition of Alkylaluminum on the Copolymerization of Styrene and Ethylene with the CpTi(OPh)$_3$/MAO Catalytic System[a]

		alkylaluminum[c]			comp of copolym products (wt %)		
run	MAO[b] (mM)	TMA (mM)	TIBA (mM)	activity[d] $\times 10^{-5}$	S−E copolymer[e]	SPS[f]	PE[f]
36	6.4	0	0	1.25	90.5	5.0	4.5
37	6.4	0.1	0	1.71	15.5	67.0	17.5
38	6.4	0.3	0	2.17	13.5	72.3	14.2
39	6.4	0.5	0	0.23	nd[g]	95.5	4.5
40	0	6.4	0	0	0	0	0
41	0	8.0	0	0	0	0	0
42	6.4	0	0.3	1.88	27.5	58.7	14.8
43	6.4	0	0.6	2.42	17.5	72.2	10.3
44	6.4	0	0.9	0.55	nd[g]	94.2	5.8
45	0	0	6.4	0	0	0	0
46	0	0	8.0	0	0	0	0

[a] Polymerization conditions: S/E in feed, 50/50 (mol/mol); other conditions, see Table 1. [b] Internal residual TMA content in MAO, 26.5 mol %. [c] Activity in units of g of polymer/((mol of Ti)·h). [d] External addition of alkylaluminum. [e] Calculated from the THF-soluble fraction. [f] Estimated from elemental analysis and ^{13}C NMR spectra of the THF-insoluble fraction. [g] Not detected.

scribed in butylaluminoxane).[31] Our investigation shows that MAO is a complex mixture at least containing, besides TMA, many compounds with molecular weights between 250 and 1500, in agreement with the results reported by other authors.[32,33] We have studied the effect of molecular weight of MAO on the copolymerization of styrene and ethylene. The preliminary results show that in order to get a high catalytic activity and yield of S−E copolymer, the MAO molecular weight or oligomerization degree (n) should be higher than a critical minimum, which is approximately 1000 ($n \approx 18$). In the S−E copolymerization studied, an oligomerization degree (n) of 13−16 is optimum for the formation of PE, $n = 24{-}28$ for the formation of SPS, and $n = 18{-}20$ for the formation of S−E copolymer. Although a complete understanding of the effects of MAO requires much more work, especially since the exact speciation of MAO is complex and unknown up to now, we are certain that the composition and structure of MAO studied control the structure of the active species, thus showing different coordinative selectivity for homopolymerization and copolymerization of styrene and/or ethylene in the titanocene-based catalytic system (e.g. CpTi(OPh)$_3$/MAO). Therefore, it is not surprising that there exists a contradiction in results obtained by Longo et al.[12] and Aaltonen et al.[18,19] on the copolymerization of styrene with ethylene using CpTiCl$_3$/MAO.

A very different effect was seen when certain amounts of other organoaluminum, such as trimethylaluminum (TMA) and triisobutylaluminum (TIBA), were added to the copolymerization of styrene and ethylene (Table 5). It was found that the catalytic activity increased and reached a maximum after the addition of TMA or TIBA. The yield of S−E copolymer decreased rapidly while the yield of SPS homopolymer increased progressively with the addition of either TMA or TIBA. However, the addition of TMA (0.5 mmol) or TIBA (0.9 mmol) not only prevented the copolymerization but also reduced markedly the activity of styrene homopolymerization. Addition of a given amount of TMA or TIBA (below the critical maximum) apparently inhibits certain functions of MAO to form active species of copolymerization but promotes some synergistic functions of MAO for syndiotactic polymerization of styrene. Since TMA and TIBA are stronger alkylating and thus reducing agents than MAO, the addition of TMA or TIBA could cause the reduction of Ti(IV) to Ti(III) complex, thereby promoting styrene homopolymerization but preventing the copolymerization. As a matter of fact, in the analysis of the Ti oxidation state, we found that the percentage of Ti(III), as expected, was 45.2% at Al/Ti = 800 but 90.3 and 87.7 after addition of TMA (0.1 mM) and TIBA (0.4 mM). Of course, other processes may separately or synergistically influence the copolymerization. For example, TMA or TIBA competes with MAO as a complexing ligand to change the coordinative environment and structure of active species. In addition, addition of TMA or TIBA can lower the degree of oligomerization of MAO and its effectiveness. The analogous effect was observed in ethylaluminoxane.[34] It must be pointed out that TMA or TIBA itself does not activate CpTi(OPh)$_3$ to form active species for either homopolymerization or copolymerization (Table 5), suggesting that MAO is the actual cocatalyst in the copolymerization using the metallocene/MAO catalytic system.

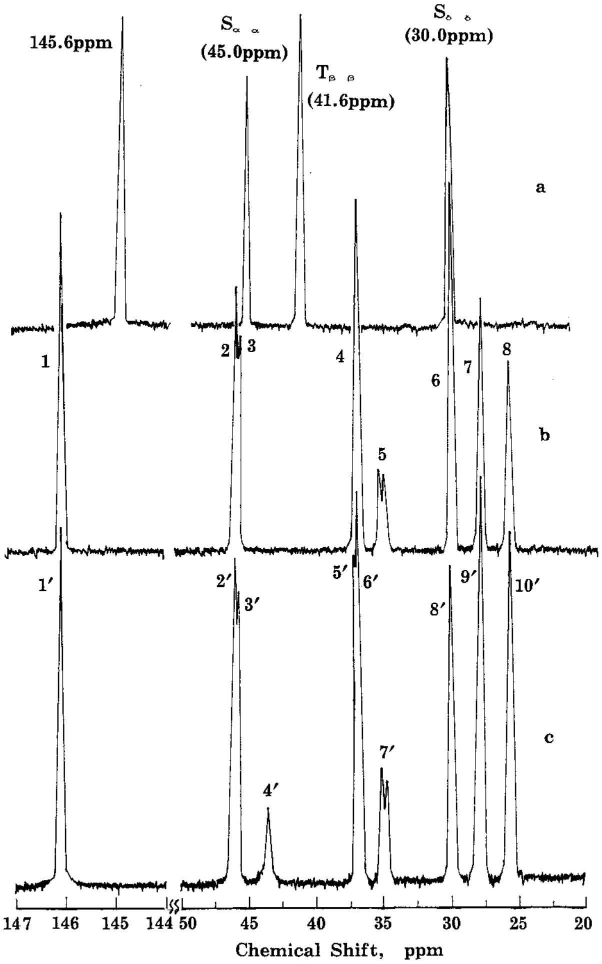

Figure 2. ^{13}C NMR spectra of styrene−ethylene copolymerization products prepared from CpTi(OPh)$_3$/MAO catalyst: (a) THF-insoluble fraction (run 4); (b) THF-soluble fraction (run 4); (c) THF-soluble fraction (run 3).

Characterization of S−E Copolymers. The copolymerization products were sequentially fractionated according to their solubility in MEK and THF solvents. The THF-insoluble fraction (THF-Insol.) and the THF-soluble fraction (THF-Sol.) were characterized by ^{13}C NMR as shown in Figure 2. In the NMR spectrum (A) of THF-Insol., only four peaks could be found at 145.6, 45.0, 41.6, and 30.0 ppm. The peak at 145.6 ppm is assigned to the phenyl C-1 carbon in syndiotactic polystyrene, and the other three peaks in the aliphatic

Table 6. Assignments of the ^{13}C NMR Chemical Shifts of the Styrene−Ethylene Copolymers[a]

sample I					sample II				
			chemical shift (ppm)					chemical shift (ppm)	
peak	carbon type	sequence	calcd	obsd	peak	carbon type	sequence	calcd	obsd
1	Ph-Cl		146.30		1′	Ph-Cl		146.30	
2	$T_{\delta\delta}$	ESE	45.90	45.89	2′	$T_{\delta\delta}$	ESE	45.90	45.89
3	$T_{\gamma\delta}$	SES	45.50	45.62	3′	$T_{\gamma\delta}$	SES	45.50	45.62
4	$S_{\alpha\gamma} + S_{\alpha\delta}$	$\underline{\text{S}}$ES + SEE	36.88	36.83	4′	$T_{\beta\delta}$	SSE	43.50	43.55
5	$S_{\alpha\beta}$	$\bar{\text{S}}$ES	34.89	35.10, 34.50	5′	$S_{\alpha\gamma} + S_{\alpha\delta}$	SES +SEE	36.88	36.83
6	$S_{\gamma\delta} + S_{\delta\delta}$	SEE$_{n\geq1}$ + ESE	29.87	29.89	6′	$S'_{\alpha\delta}$	$\underline{\text{E}}$SSE	36.89	37.05
7	$S_{\beta\delta}$	ESE, SEE$_{n\geq1}$	27.87	27.73	7′	$S_{\alpha\beta}$	$\bar{\text{S}}$ES	34.89	35.10,34.50
8	$S_{\beta\beta}$	SES	25.87	25.51	8′	$S_{\gamma\delta} + S_{\delta\delta}$	SEE$_{n\geq1}$ + ESE	29.87	29.89
					9′	$S_{\beta\delta}$	ESE, SEE$_{n\geq1}$	27.87	27.73
					10′	$S_{\beta\beta}$	SES	25.87	25.51

[a] Sample I contains 29.7 mol % styrene incorporation (run 4), but sample II contains 44.1 mol % styrene incorporation (run 3).

carbon region are assigned to $S_{\alpha\alpha}$ and $T_{\beta\beta}$ in the syndiotactic styrene sequence (45.0 and 41.6 ppm, respectively) and $S_{\delta\delta}$ in the ethylene sequence (30.0 ppm). These findings indicate that the THF-insoluble fraction is a mixture of syndiotactic polystyrene and polyethylene homopolymer.

However, the NMR spectrum of the THF-soluble fraction of the copolymerization products, obtained by changing the comonomer feed ratio in Table 1, was quite different from that of the THF-insoluble fraction. In the ^{13}C NMR spectrum (B) of THF-Sol. containing 29.7 mol % styrene incorporation (sample I) in run 4 of Table 1, a resonance peak at 29.89 ppm, although it is almost coincident with that of $S_{\delta\delta}$ carbon in the ethylene sequence (30.0 ppm) of polyethylene, can be assigned to $S_{\gamma\delta}$ in S−E copolymer having isolated styrene units in the sequence. Other resonance peaks observed at 25.51, 27.73, 36.83, 45.62, and 45.89 ppm in the aliphatic region can be assigned respectively to $S_{\beta\beta}$, $S_{\beta\delta}$, $S_{\alpha\gamma}$, $S_{\alpha\delta}$, $T_{\gamma\delta}$, and $T_{\delta\delta}$ in the copolymer sequence according to the improved Grant and Paul empirical method through calculated chemical shifts.[35] All these patterns of resonances are diagnostic of a styrene−ethylene copolymer containing SEE, SES, and ESE sequences as shown in Table 6. The resonances detected at 34.50 and 35.10 ppm are attributable to $S_{\alpha\beta}$, which is due to an ethylene unit bridging head-to-head arranged S units ($\bar{\text{S}}$ES sequence). The diagnostics of the $\bar{\text{S}}$ES sequence in the copolymer show that the insertion of styrene is not completely regioregular using homogeneous CpTi(OPh)$_3$/MAO catalyst. That is to say there exists either a secondary insertion or primary insertion of styrene in the copolymerization of styrene and ethylene. This chemical inversion of styrene units was also observed in the same copolymerization system using the [(methyl)(phenyl)methylene(1-cyclopentadienyl)(9-fluorenyl)]zirconium dichloride/MAO catalytic system.[15] From these findings, the peak at 146.30 ppm can be assigned to the phenyl C-1 carbon attached to the $T_{\delta\delta}$ and $T_{\gamma\delta}$ carbons in the copolymer.

In the ^{13}C NMR spectrum (C) of THF-Sol. containing 44.1 mol % styrene incorporation (sample II), obtained at high styrene concentration in run 3 of Table 1, in addition to the resonances previously assigned to the SEE, SES, ESE, and $\bar{\text{S}}$ES sequences in sample I, one can observe the signals at 43.55 and 37.05 ppm attributable respectively to the $T_{\beta\delta}$ and $S'_{\alpha\delta}$ carbons in the S−E copolymer containing the ESSE sequence (see Table 6). The relatively weak peak at 43.55 ppm observed only in samples containing higher comonomer incorporation (44.1 and 54.5 mol %) indicates presumably the formation of a very small amount of blocks of two comonomeric units. The appearance of an additional peak at 37.05 ppm for these samples which can plausibly be assigned to the $S'_{\alpha\delta}$ of the blocks confirms their formation. In addition, it was found that the intensity of the resonances due respectively to chemical inversion of styrene units and block sequence became more and more strong with increasing styrene incorporation in the copolymer.

On the other hand, it was found that the spectrum of the THF-soluble fraction of the copolymerization product in run 21 of Table 3, obtained in the presence of a mole ratio of CpTi(OPh)$_3$/MAO = 1:600, was very similar to that of the THF-soluble fraction in run 4, the only difference being the larger intensity of the quoted resonances. However, the spectrum of the THF-soluble fraction of the copolymerization products in run 23, obtained in the presence of a mole ratio of CpTi(OPh)$_3$/MAO = 1:1000, was very similar to that of the THF-soluble fraction in run 3, the only difference being the larger intensity of the resonance of the SSE sequence. These findings suggest that the microstructure of the copolymers is strongly dependent on both the comonomer feed ratio and the CpTi(OPh)$_3$/MAO molar ratio.

DSC measurements of the copolymers containing different styrene incorporation from 18.5 to 54.5 mol % (runs 2−6) were conducted with a Perkin-Elmer DSC-2 system, and a single glass transition (T_g), which is different from that of SPS of PE homopolymer, was detectable in the heating curves as shown in Figure 3. It is clearly seen that the glass transition peak continuously moves to higher temperatures from 15.8 to 35.5 °C as styrene incorporation in the copolymers increases. When compared with homopolymers, the melting points (T_m) of the copolymers obtained are not detected by DSC, no matter how high the comonomer incorporation in the copolymers is. The melting point (T_m) and crystallinity are attributed to a unique blocky microstructure which offers enough consecutive sequences of comonomer units in the polymer backbone to form a crystalline phase. Apparently, the produced styrene−ethylene copolymers do not have such a blocky microstructure. The wide-angle X-ray diffraction patterns of the copolymers do not display any crystalline reflection in the $2\theta = 4-40°$ range (Figure 4), in agreement with the DSC results. Together with ^{13}C NMR analysis, it is more likely that the copolymer with higher monomer incorporation has such a short-range block of regioregularly arranged E−E or S−S sequence that it cannot form a crystalline phase. The investigation of the mechanical properties shows that the S−E copolymer obtained is an elastoplastic.

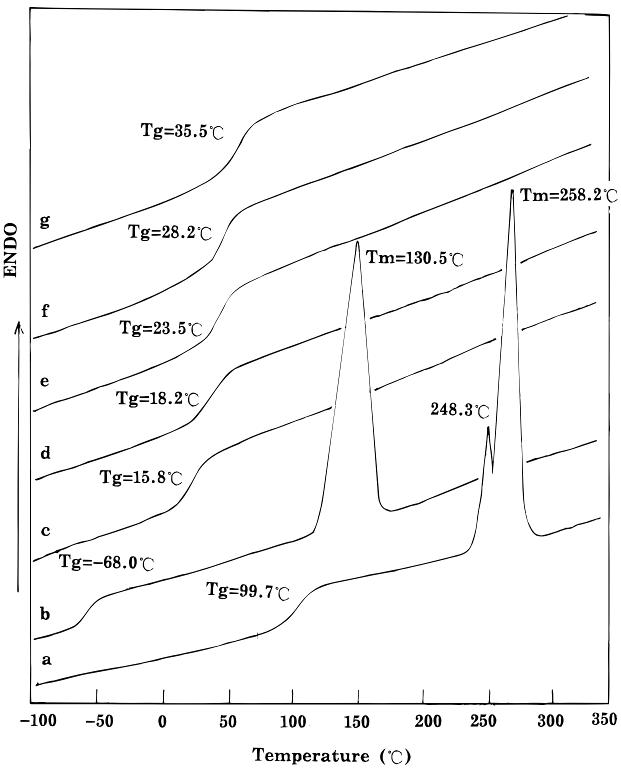

Figure 3. DSC diagram of homopolymers and S−E copolymers obtained by using CpTi(OPh)$_3$/MAO catalyst: (a) SPS; (b) PE; (c) S−E copolymer (St = 18.5 mol %); (d) S−E copolymer (St = 23.3 mol %); (e) S−E copolymer (St = 29.7 mol %); (f) S−E copolymer (St = 44.1 mol %); (g) S−E copolymer (St = 54.5 mol %).

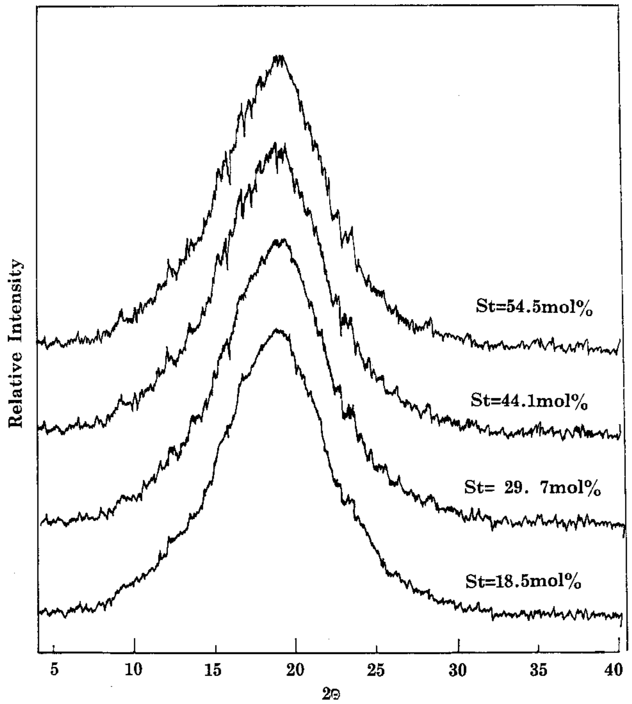

Figure 4. Wide-angle X-ray scattering curves for S−E copolymers with various compositions.

Conclusions

The titanocene-based catalytic system of CpTi(OPh)$_3$/MAO is able to promote the copolymerization of styrene and ethylene with higher catalytic activity, depending upon the cocatalyst MAO (including the Al/Ti mole ratio,the TMA content in MAO, and the composition and structure of MAO) and polymerization conditions (comonomer feed ratio and polymerization temperature). As can be seen, there is a critical amount of MAO, TMA content, and molecular weight (or oligomerization degree) in MAO below which no copolymerization occurs. However, the effects of the composition and structure of MAO on the nature of the active species in the copolymerization of styrene and ethylene require more study. The addition of TMA or TIBA can promote styrene homopolymerization but inhibit the copolymerization of styrene with ethylene. The results obtained by combining ESR spectroscopic analysis with polymerization data suggest that, in the S−E copolymerization, an active species, a cationic titanium Ti(IV) complex, is responsible for promoting ethylene polymerization, that a second active species, a Ti(III) complex, is favorable for promoting styrene syndiospecific homopolymerization, and that a third, possibly intermediate complex, is able to promote the copolymerization of styrene and ethylene.

The copolymerization by CpTi(OPh)$_3$/MAO catalyst produces both a THF-soluble fraction, which is a styrene−ethylene copolymer, and a THF-insoluble fraction, which is a mixture of PE and SPS homopolymers. As investigated by ^{13}C NMR, DSC, and WAXD, the S−E copolymers are confirmed to be elastoplastic and amorphous random/alternating copolymers, along with chemical inversion of styrene units, with a single glass transition (T_g) but without a melting transition (T_m), no matter how high the comonomer incorporation in the copolymer is.

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