

## 1. General Experimental Procedure

**General Procedure.** All synthetic experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques unless otherwise specified. All chemicals used were reagent grade and were purified by the standard purification procedures. Toluene for the polymerization was distilled over sodium and benzophenone under nitrogen atmosphere, and was stored in a Schlenk tube in the drybox in the presence of molecular sieves (mixture of 3A and 4A 1/16, and 13X). Reagent grade of styrene was distilled under nitrogen in the presence of  $\text{CaH}_2$  after the standard purification procedure, and was stored in a Schlenk tube under  $\text{N}_2$  in the freezer. Ethylene for polymerization was of polymerization grade (purity >99.9%, Sumitomo Seika Co. Ltd.) and was used as received. Syntheses of  $\text{Cp}'\text{TiCl}_2(\text{OAr})$  [ $\text{Cp}' = \text{Cp}$  (**1a**),  $^i\text{BuC}_5\text{H}_4$  (**2a**), 1,3- $\text{Me}_2\text{C}_5\text{H}_3$  (**3a**), 1,3- $^i\text{Bu}_2\text{C}_5\text{H}_3$  (**4a**),  $\text{C}_5\text{Me}_5$  (**5a**), and  $\text{OAr} = \text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$ ] complexes were according to our previous report. Toluene and  $\text{AlMe}_3$  in the commercially available methylaluminoxane (PMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Akzo Co.) were removed and dried *in vacuo* in the drybox, and used as a white solid.

All  $^1\text{H}$ - and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz,  $^1\text{H}$ ; 100.40 MHz,  $^{13}\text{C}$ ). All chemical shifts are given in ppm and are referenced to tetramethylsilane. Obvious multiplicities and routine coupling constants are usually not listed, and all spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. All deuterated NMR solvents were stored over molecular sieves.  $^{13}\text{C}$ -NMR spectra for the poly(ethylene-*co*-styrene)s were performed by using JEOL LA400 spectrometer ( $\text{CDCl}_3$ ) with proton decoupling at 60 °C. The pulse interval was 5.2 sec, the acquisition time was 0.8 sec, the pulse angle was 90°, and the number of transients accumulated was ca. 10000.  $^1\text{H}$  NMR spectra for the copolymer (calculation of styrene content in the copolymer) were measured in the same manner (tetrachloroethane- $d_4$ ) at 100 °C. The polymer solutions were prepared by dissolving polymers in solvent up to 10% by weight.

Molecular weight and molecular weight distribution of the resultant copolymers were

measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with polystyrene gel column (TSK gel GMH<sub>HR</sub>-H HT x 2) at 140 °C using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*-butyl-*p*-cresol as solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples. Differential scanning calorimetric (DSC) data for the copolymer were recorded by means of DSC6100 (Seiko Instruments Co.) under nitrogen atmosphere [conditions: heating from 25 to 300 °C (20 °C/min), cooling from 300 to -100 °C (10 °C/min)].

**Synthesis of (1,3-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>)TiCl<sub>2</sub>(O-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (3b).** LiO-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (287 mg, 2.24 mmol) was added in one portion to a Et<sub>2</sub>O solution (30 mL) containing (1,3-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>)TiCl<sub>3</sub> (555 mg, 2.24 mmol) at -30 °C. The reaction mixture was warmed slowly to room temperature, and was stirred for 10 h. The mixture was then filtered through Celite, and the filter cake and was washed with Et<sub>2</sub>O. The combined filtrate and the wash were taken to dryness under reduced pressure to give an orange solid. The solid was then dissolved in a minimum amount of CH<sub>2</sub>Cl<sub>2</sub> layered by a small amount of *n*-hexane. The chilled (-30 °C) solution gave orange microcrystals (550 mg, 1st crop). The microcrystals were pure enough by <sup>1</sup>H and <sup>13</sup>C NMR, and by elemental analysis. Yield 78 %. The second crop would increase the yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.28 (s, 6H), 2.35 (s, 6H), 6.23 (d, 2H, *J* = 2.4 Hz, Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>), 6.40 (t, 1H, *J* = 2.4 Hz, Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>), 6.86 (t, 1H, *J* = 7.6 Hz, C<sub>6</sub>H<sub>3</sub>), 6.98 (d, 2H, *J* = 7.8 Hz, C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 16.7, 17.2, 120.6, 122.2, 123.6, 127.9, 128.4, 136.8, 165.2. Anal. Calcd. for C<sub>15</sub>H<sub>18</sub>Cl<sub>2</sub>OTi: C, 54.09; H, 5.80. Found (1): C, 54.14; H, 5.44; N, 0.03. Found (2): C, 54.13; H, 5.45; N, 0.03.

**Synthesis of (1,3-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>)TiCl<sub>2</sub>(O-3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (3c).** The synthetic procedure of **3c** was the same as that in **3b** except LiO-3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (304 mg, 2.37 mmol), and (1,3-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>)TiCl<sub>3</sub> (587 mg, 2.37 mmol) were used. Yield 565 mg (1st crop, 78 %). The second crop would increase the yields. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.24 and 2.28 (6H), 2.30 and 2.35 (6H), 6.33-6.39 (m, 3H), 6.57-6.61 (d or m, 2H), 6.67-6.71 (d or m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 16.6, 21.2, 116.2, 120.8, 122.3, 125.8, 136.4, 139.1, 167.3. Anal. Calcd. for

$C_{15}H_{18}Cl_2OTi$ : C, 54.09; H, 5.80. Found: C, 53.90; H, 5.38; N, 0.01.

**Typical Reaction Procedure for Polymerization of Styrene.** MAO was added in a round-bottom flask (25 mL) connected to three-way valves under  $N_2$ , and the polymerization was started by the addition of styrene (4.58 mL) and a toluene solution containing titanium complex (0.83  $\mu$ mol, 2.0  $\mu$ mol/mL-toluene). The reaction mixture was stirred for 10 or 30 min at room temperature, and the polymerization was terminated with the addition of ethanol. The reaction product was extracted with chloroform, and the extract was washed with HCl aqueous solution and then rinsed with water. The chloroform extract was then poured into an excess amount of ethanol to collect white precipitate. The resultant solid was dried, and was then separated into two fractions by washing with methyl ethyl ketone (MEK) as the extraction solvent. From the  $^1H$  NMR and  $^{13}C$  NMR spectrum, it was revealed that MEK soluble fraction was atactic polymer and MEK insoluble polymer was syndiotactic polymer. It was also revealed that MEK soluble fraction was the polymer prepared only by MAO.

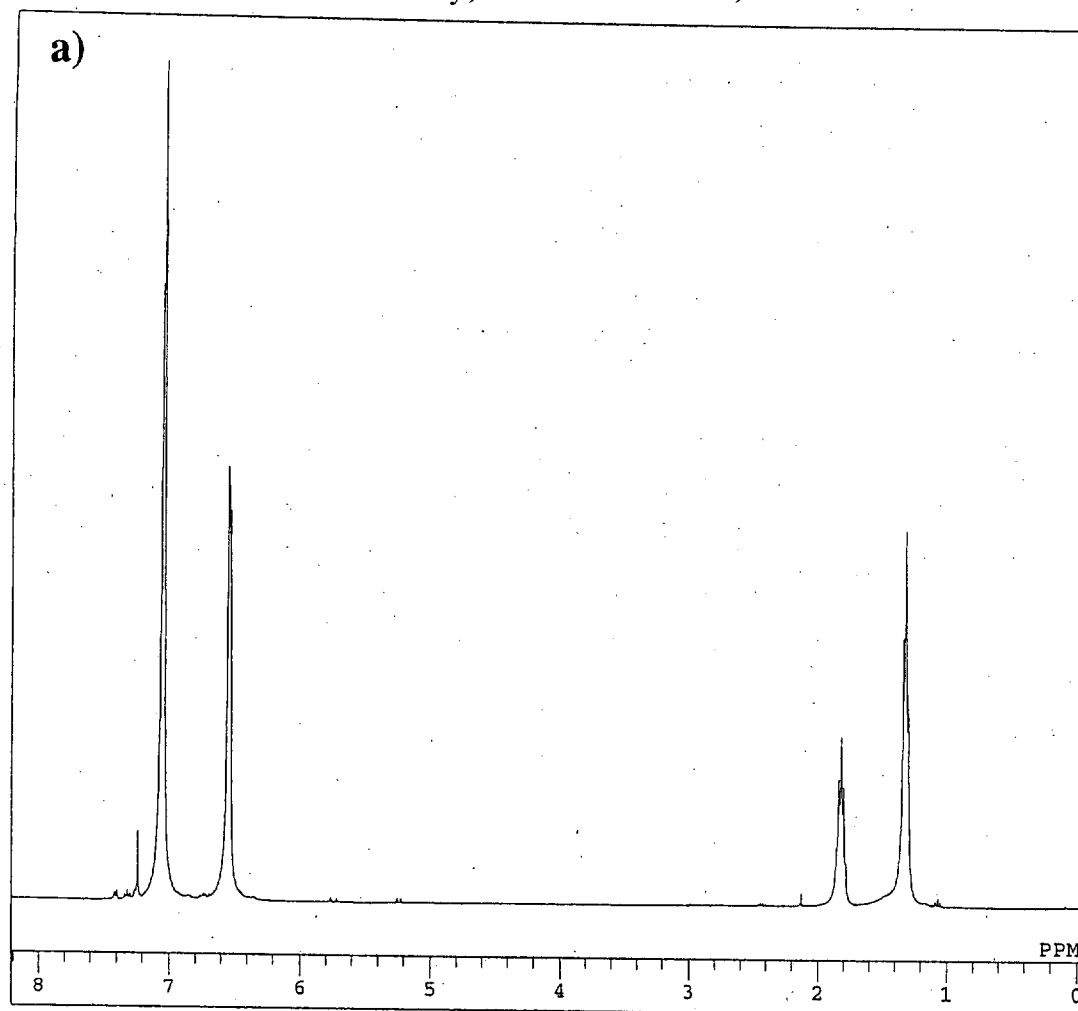
**Typical Reaction Procedure for Copolymerization of Ethylene with Styrene by (1,3- $Me_2C_5H_3$ ) $TiCl_2$ (O-2,6- $iPr_2C_6H_3$ ) (3a) - MAO catalyst.** Typical example (run 8) is as follows: toluene (24.5 mL), MAO were added into the autoclave (100 mL, stainless steel) in the drybox, and the reaction apparatus was then replaced with ethylene. The reaction mixture was then pressurized to the prescribed ethylene pressure soon after the addition of styrene and a toluene solution containing **3a**. The mixture was stirred for 10 min, and the polymerization was terminated with the addition of EtOH (15 mL). The solution was then poured into EtOH (100 mL), and the resultant polymer was adequately washed with EtOH and then dried *in vacuo* for several hours.

According to the previous report, the resultant polymer mixture was separated into three fractions, and atactic polystyrene (containing trace amount of polyethylene observed by  $^1H$  NMR) which was prepared only by MAO was extracted with acetone. Poly(ethylene-*co*-styrene) was extracted with THF, and polyethylene and polystyrene which were the by-product in this reaction was separated as THF insoluble fraction. The basic

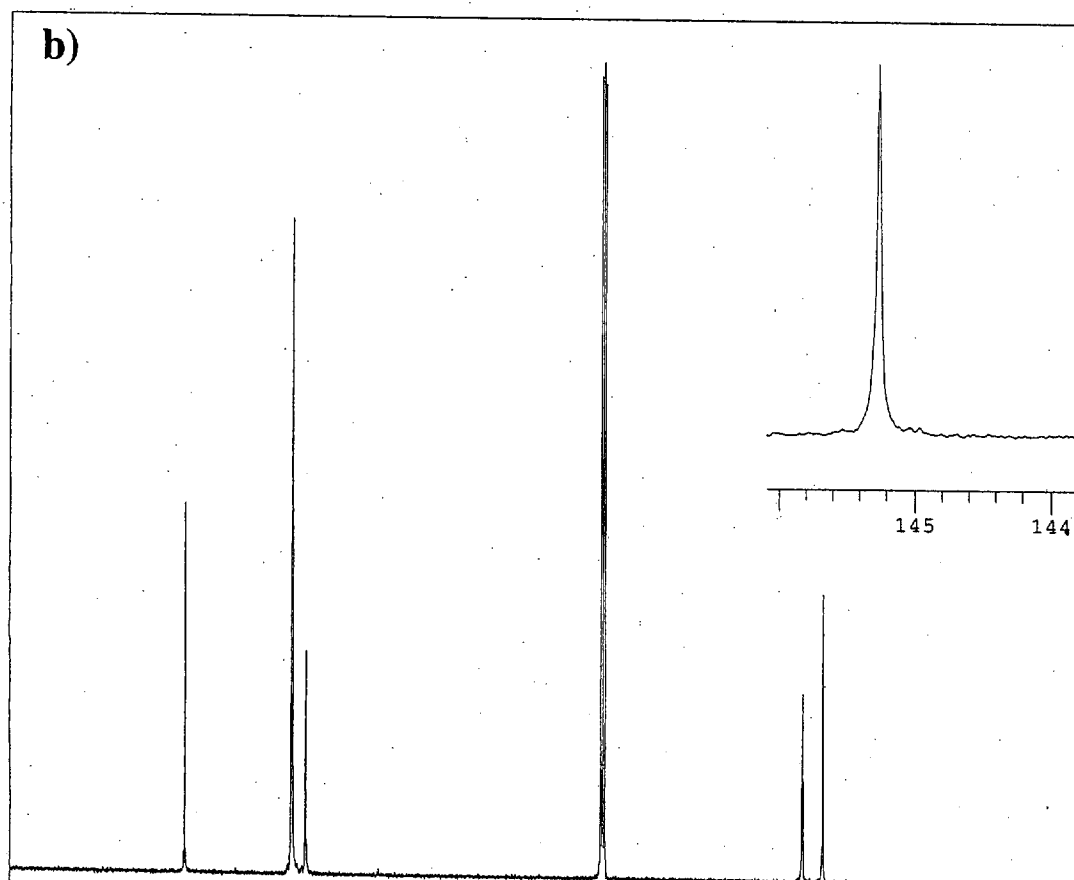
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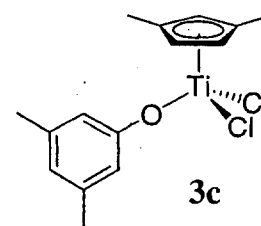
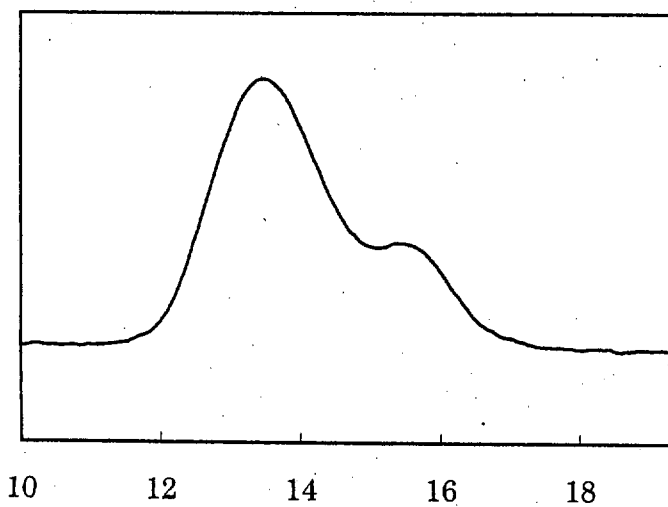
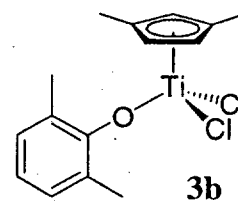
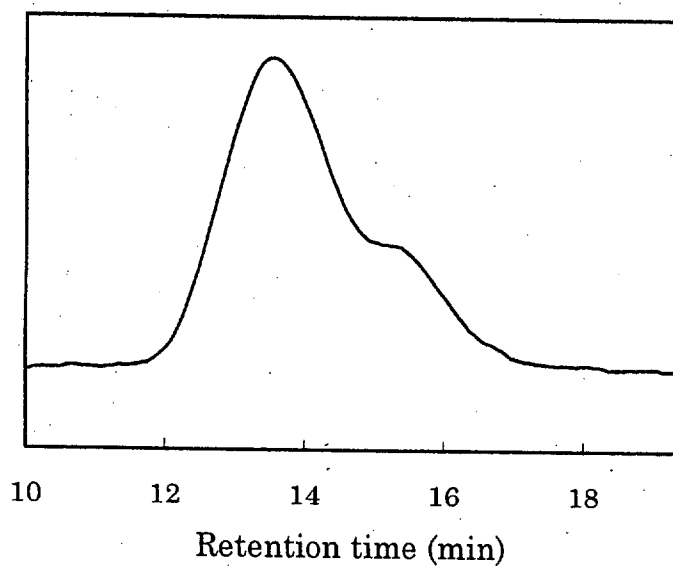
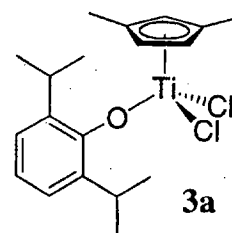
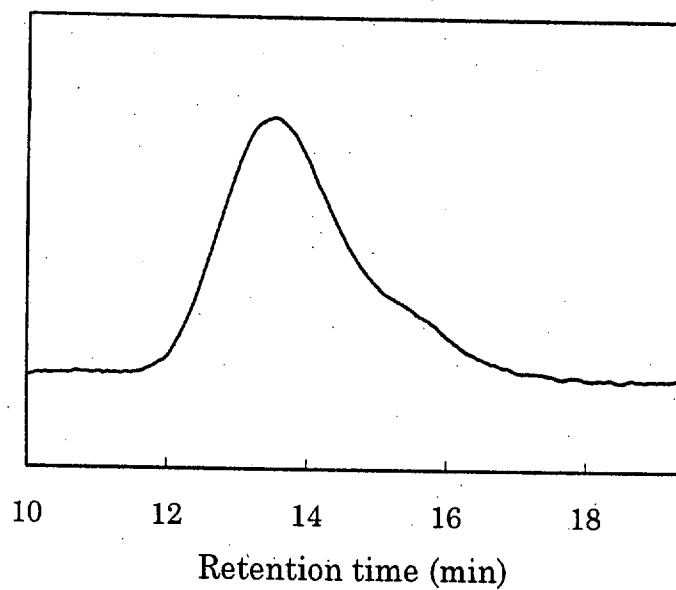
experimental procedure is as follows:

The polymer sample obtained in the copolymerization experiment was added into a round bottom flask containing acetone (100 mL) equipped with a reflux condenser, and the mixture was refluxed for 6 hours to separate acetone soluble and insoluble fractions. Then the acetone insoluble fraction was dried and added into a round bottom flask containing tetrahydrofuran (THF, 100 mL) equipped with a reflux condenser, the mixture was refluxed for 6 hours to separate THF soluble and insoluble fractions. These fractions were analyzed by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and GPC and DSC.

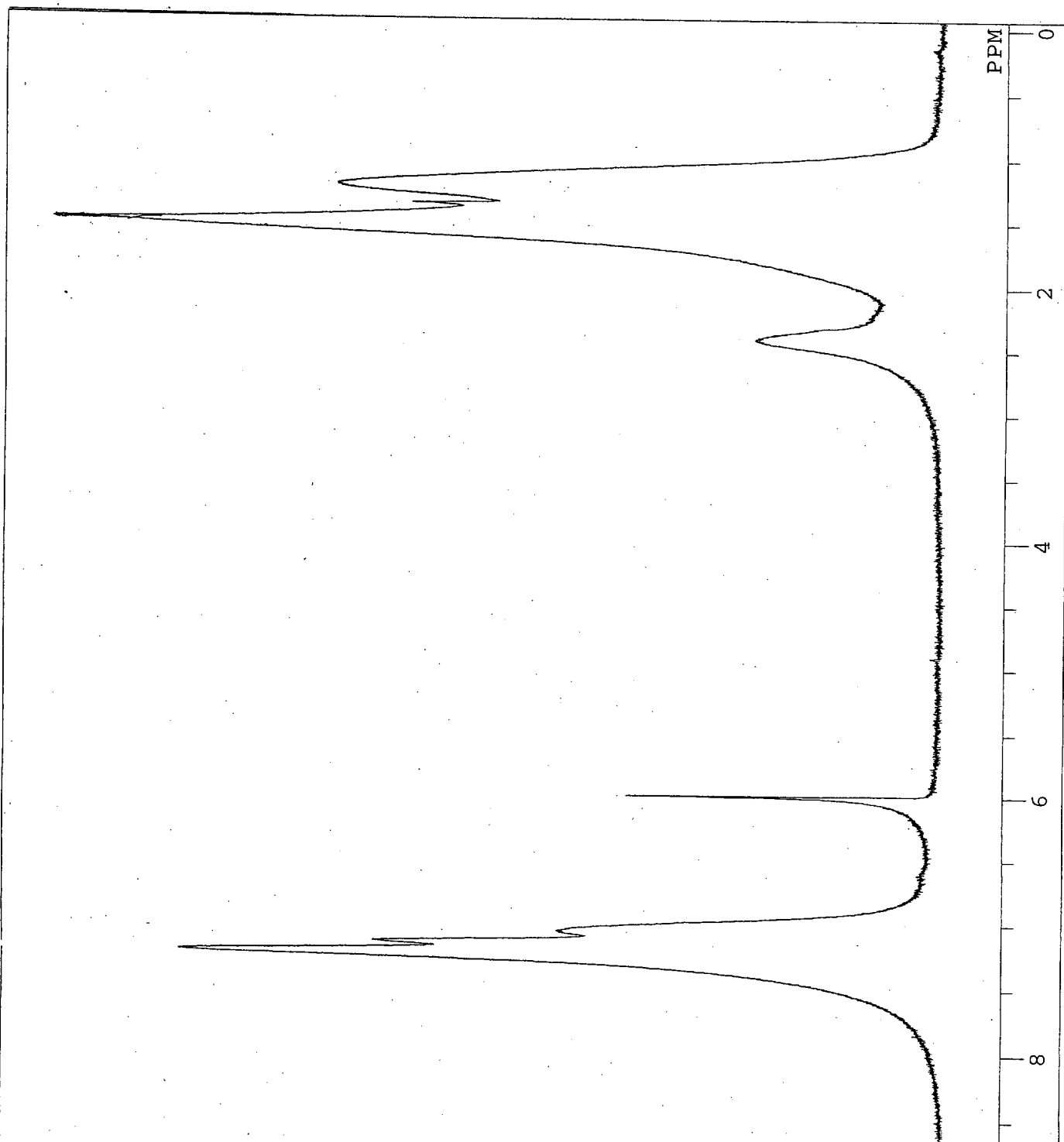


a)  $^1\text{H}$  and b)  $^{13}\text{C}$  NMR spectra (in  $\text{CDCl}_3$  at  $50^\circ\text{C}$ ) for polystyrene (methyl ethyl ketone insoluble fraction) prepared by (1,3- $\text{Me}_2\text{C}_5\text{H}_3$ ) $\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$  (**3a**) - MAO catalyst.

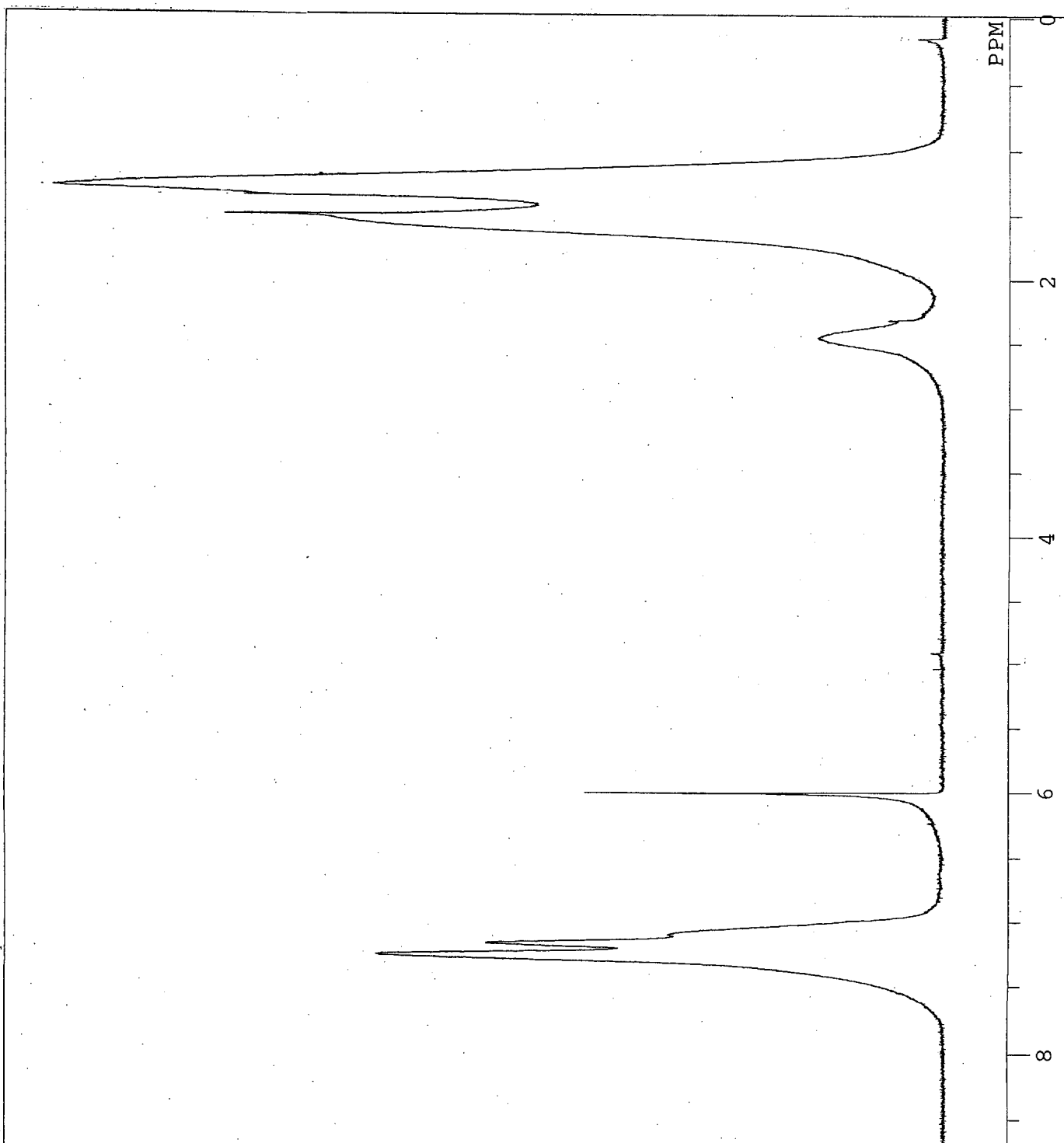




$^1\text{H}$  NMR spectrum for poly(ethylene *g*-styrene) (THF soluble fraction in tetrachloroethane- $d_2$  at 100 °C) prepared by (1,3- $\text{Me}_2\text{C}_3\text{H}_3$ ) $\text{TiCl}_2(\text{O}-2\text{-Pr}_2\text{C}_6\text{H}_3)$  (**3a**) - MAO catalyst system (ethylene 4 atm, styrene 5 mL, run 8, Table 2.)

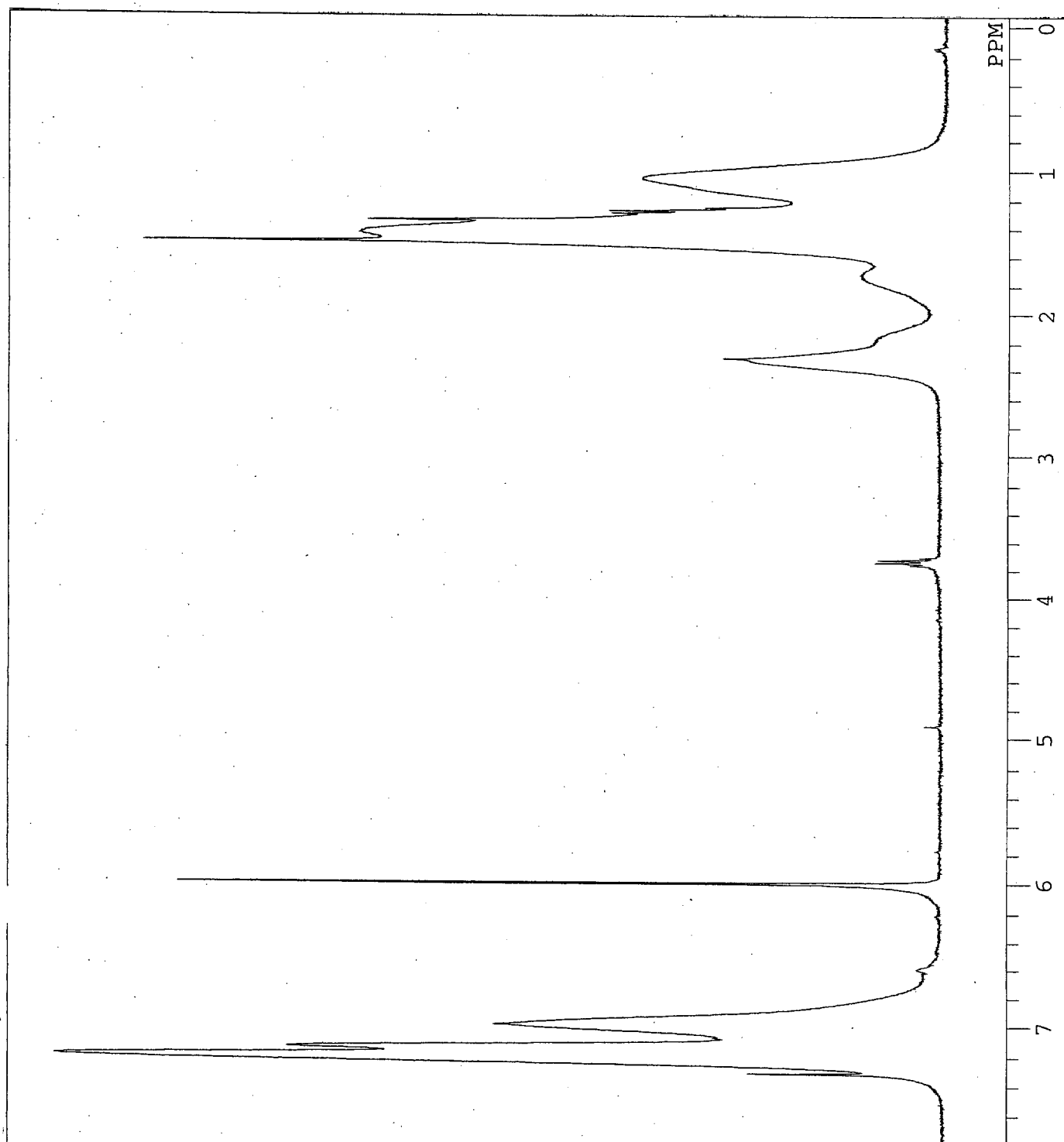


$^1\text{H}$  NMR spectrum for poly(ethylene-co-styrene) (THF soluble fraction in tetrachloroethane- $d_2$  at 100 °C) prepared by (1,3- $\text{Me}_2\text{C}_3\text{H}_3$ ) $\text{TiCl}_2(\text{O}-2,6-\text{Pr}_2\text{C}_6\text{H}_3)$  (**3a**) - MAO catalyst system. (ethylene 8 atm, styrene 5 mL, run 9, Table 2.)

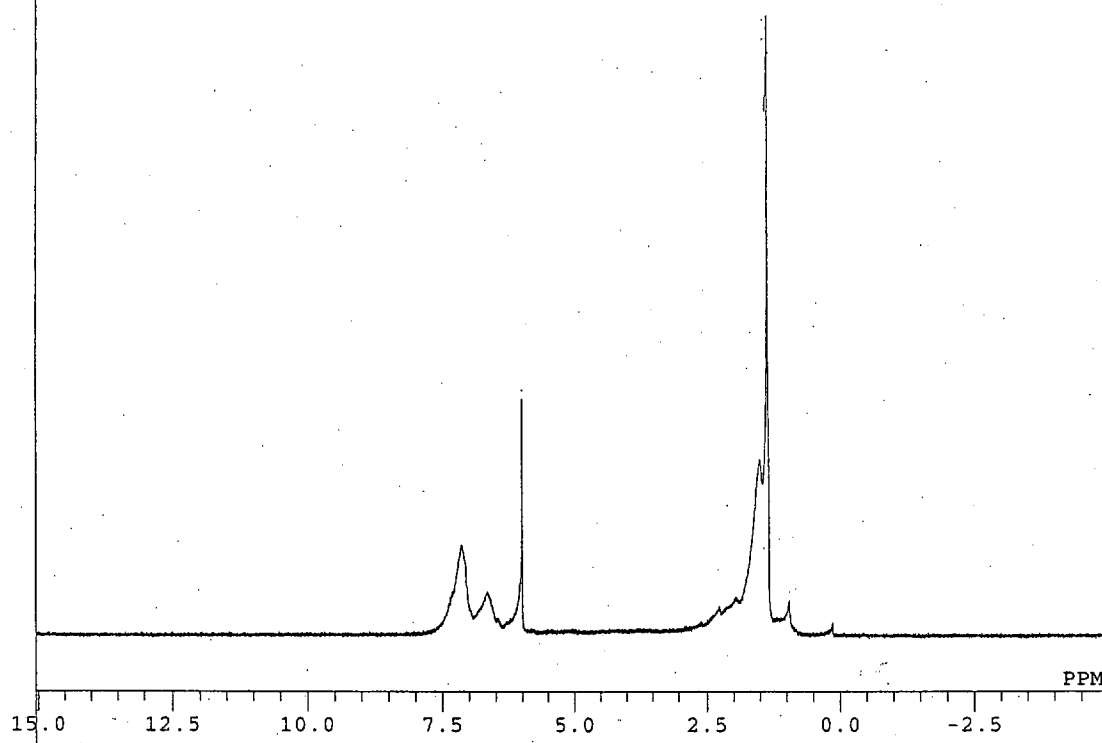




<sup>1</sup>H NMR spectrum for poly(ethylene-*d*<sub>2</sub>-styrene) (THF soluble fraction in tetrachloroethane-*d*<sub>2</sub> at 100 °C) prepared by (1,3-Me<sub>2</sub>C<sub>3</sub>H<sub>3</sub>)TiCl<sub>2</sub>(O-2-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (**3a**) - MAO catalyst system (ethylene 3 atm, styrene 10 mL, run 1 Table 2.)

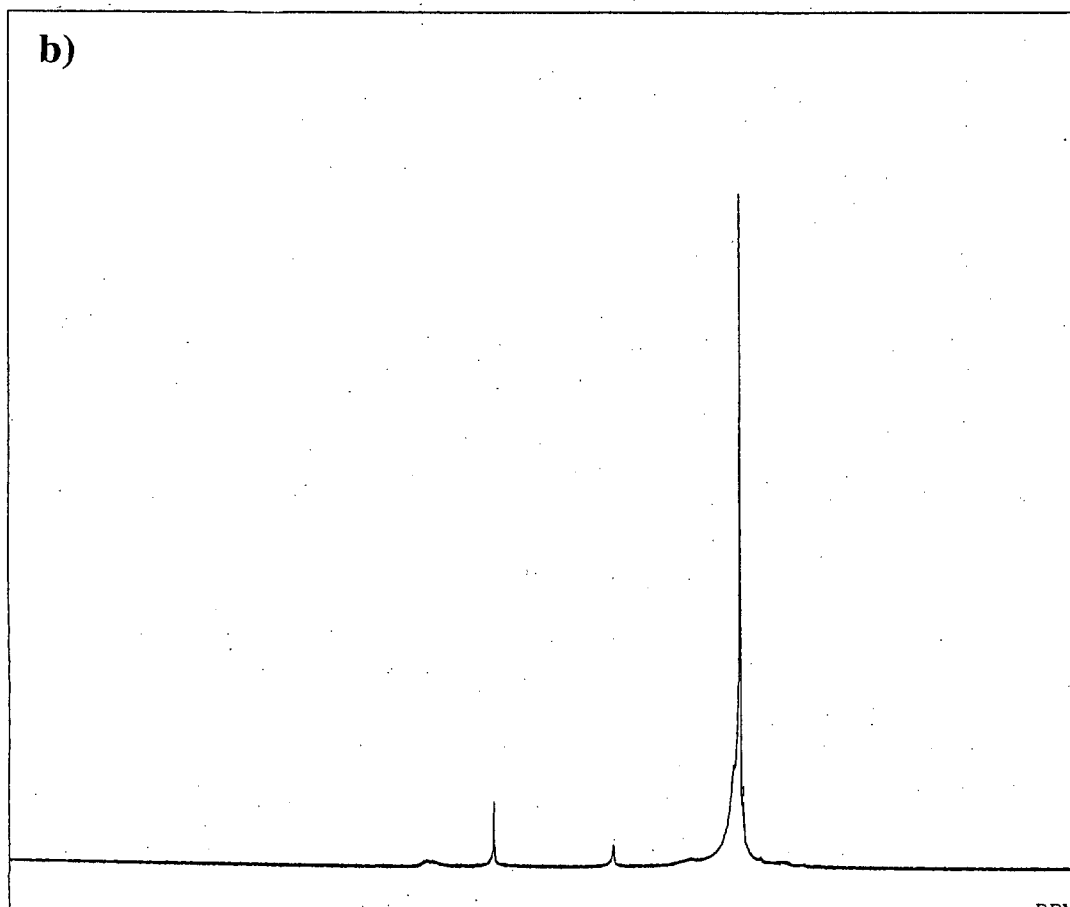


a)

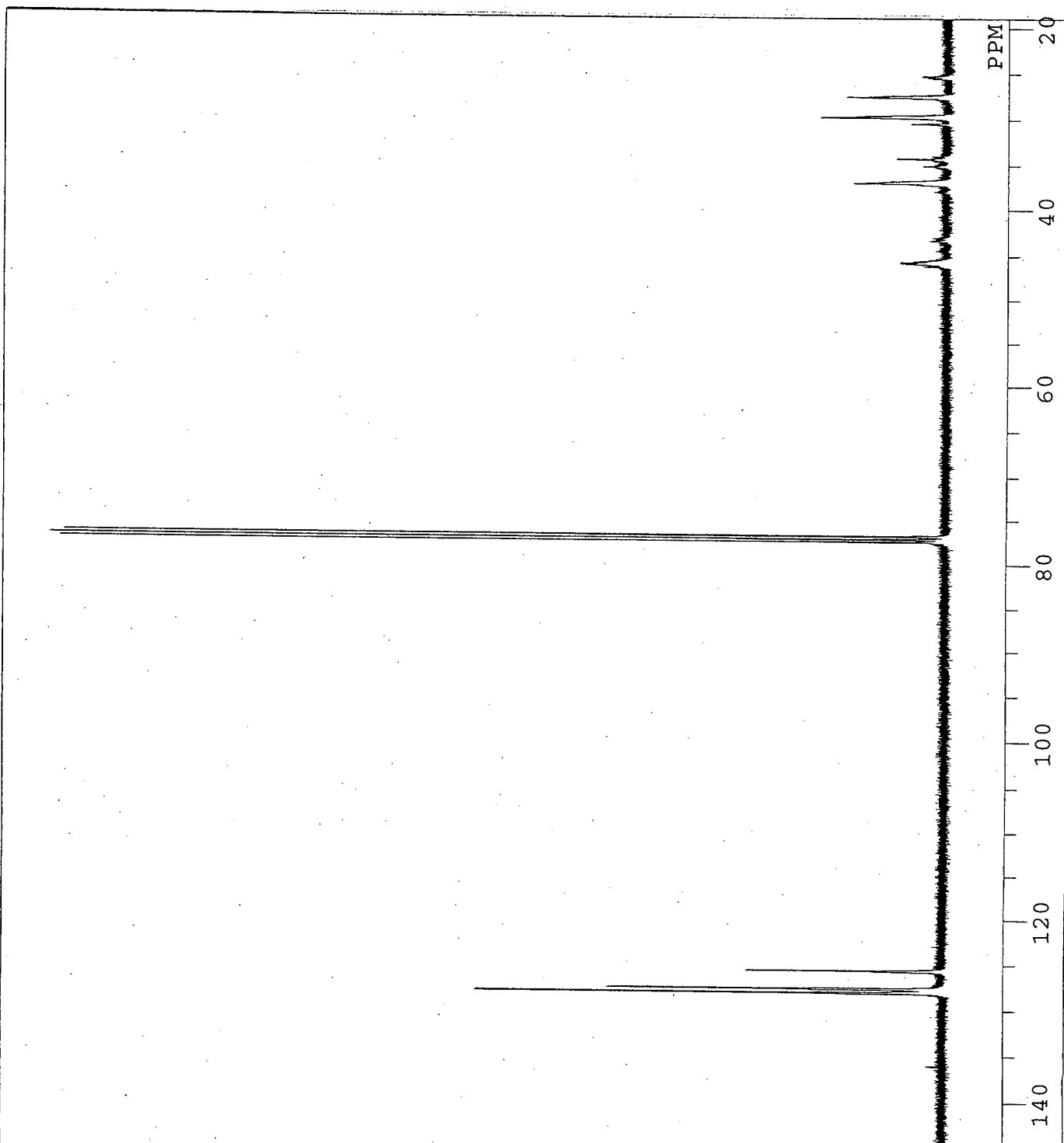


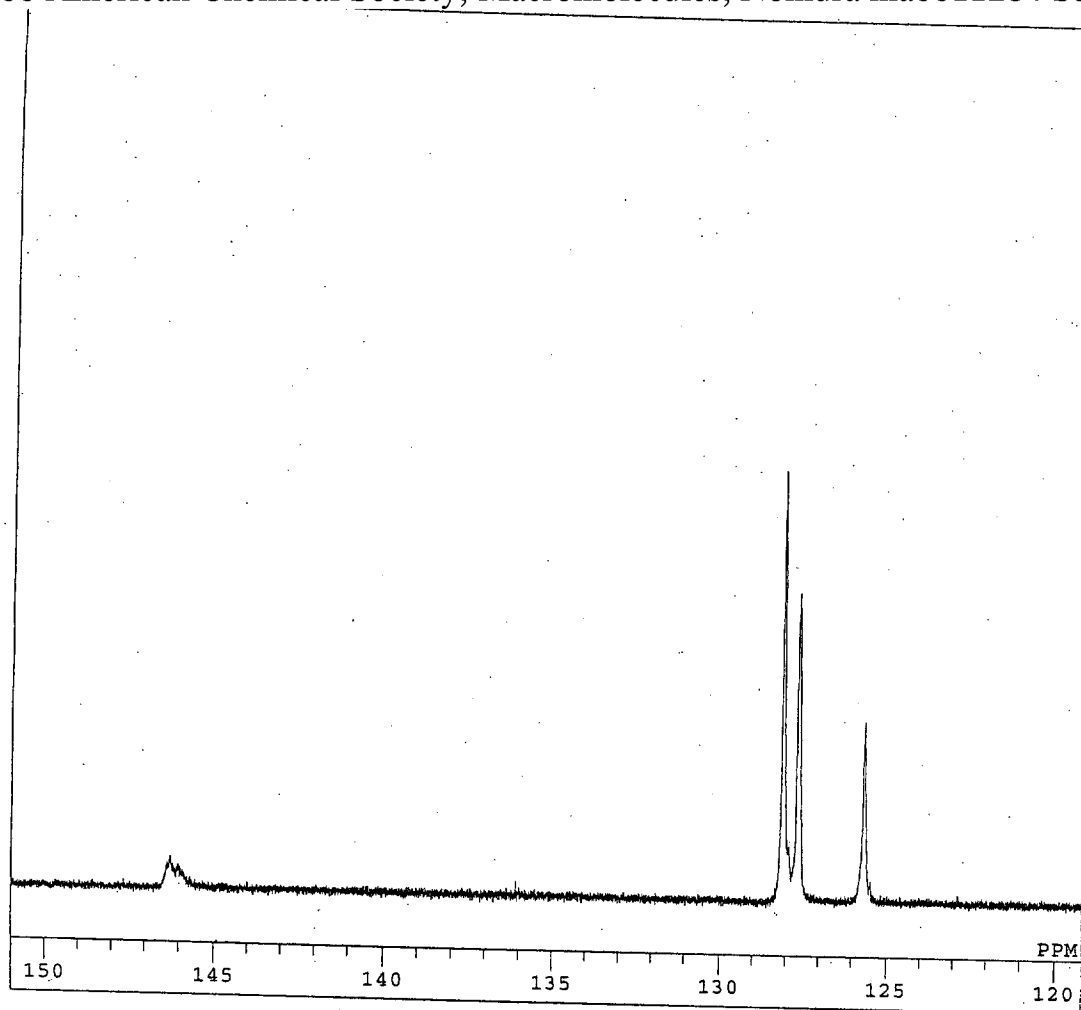
$^1\text{H}$  NMR spectra for polymers prepared by copolymerization of ethylene with styrene catalyzed by (1,3- $\text{Me}_2\text{C}_5\text{H}_3$ ) $\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$  (**3a**) - MAO system. a) acetone soluble fraction, and b) THF insoluble fraction (ethylene 8 atm, styrene 5 mL, run 9 in Table 2).

b)

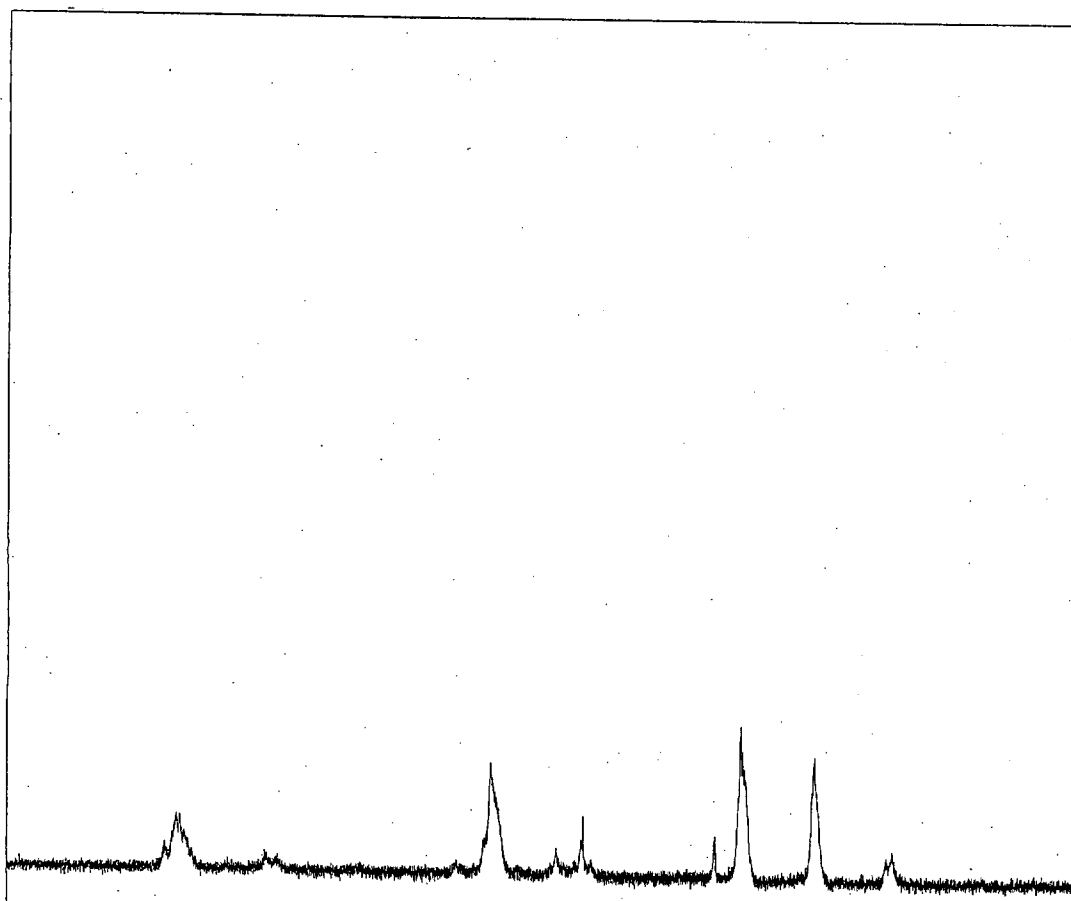


$^{13}\text{C}$  NMR spectrum for poly(ethylene *co*-styrene) (THF soluble fraction in  $\text{CDCl}_3$  at  $60^\circ\text{C}$ ) prepared by (1,3- $\text{Me}_2\text{C}_3\text{H}_3$ ) $\text{TiCl}_2(\text{O}-2,6\text{-iPr}_2\text{C}_6\text{H}_3)$  (**3a**) MAO catalyst system. (ethylene 4 atm, styrene 5 mL, run 8, Table 2.)

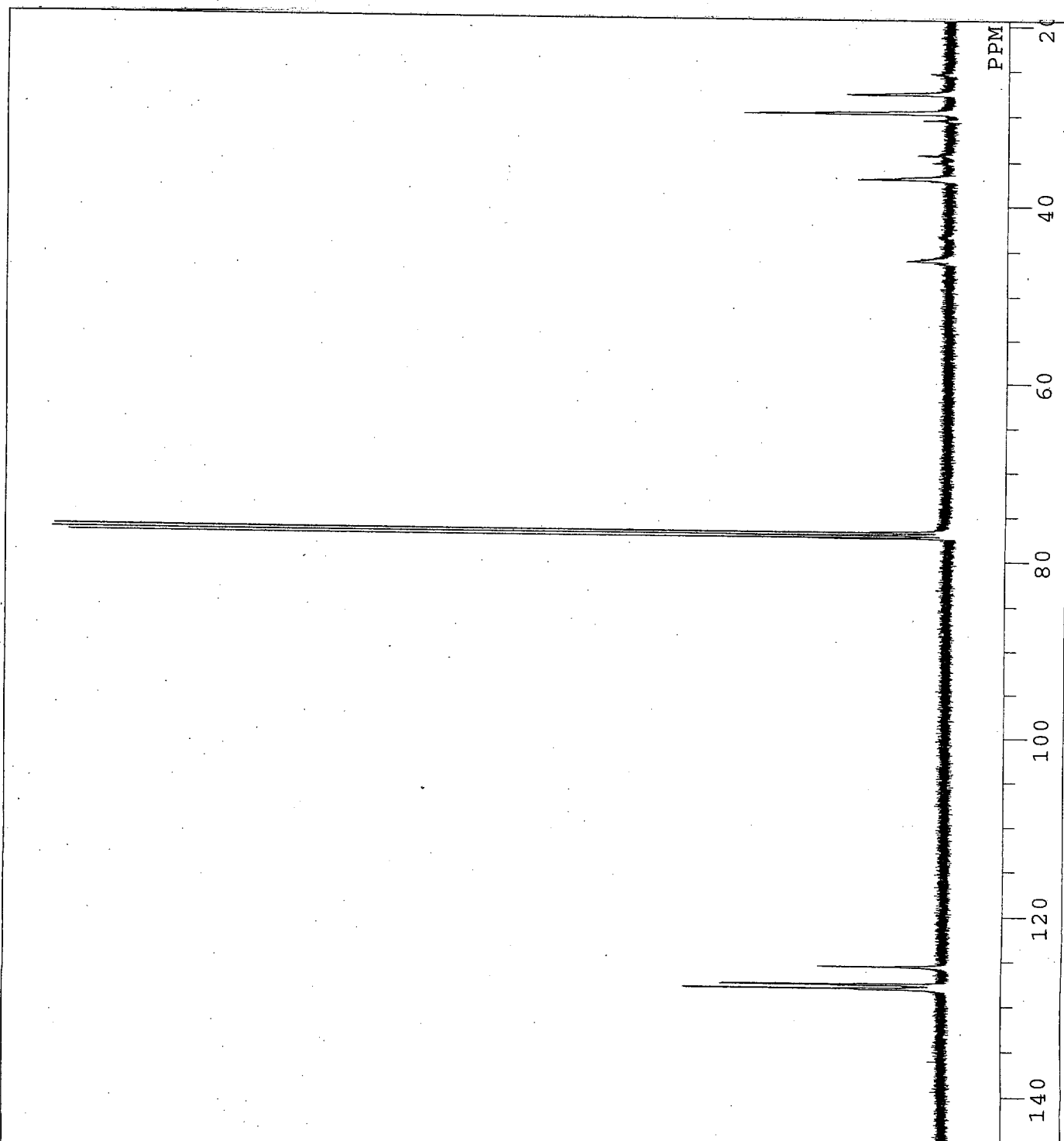


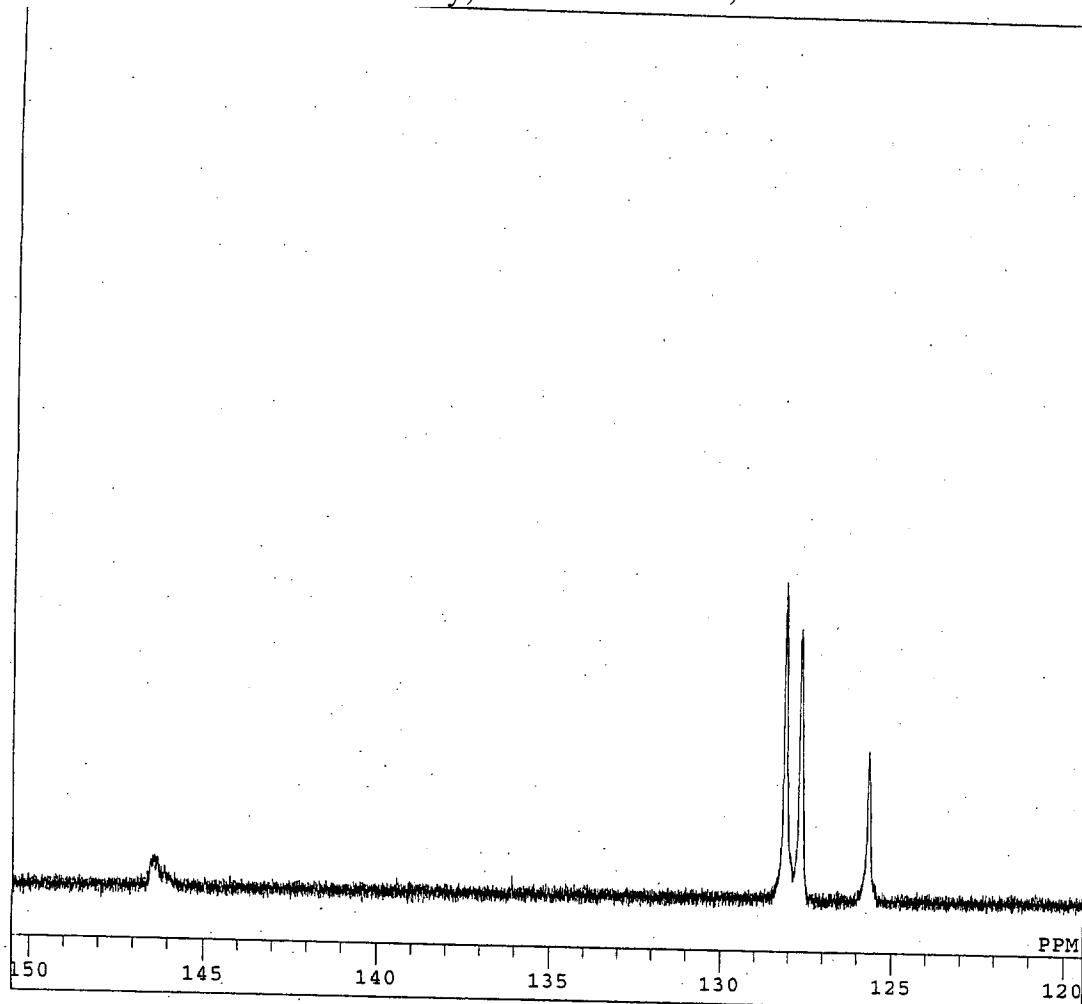


$^{13}\text{C}$  NMR spectrum for poly(ethylene-*co*-styrene) (THF soluble fraction in  $\text{CDCl}_3$  at  $60^\circ\text{C}$ ) prepared by (1,3- $\text{Me}_2\text{C}_5\text{H}_3$ ) $\text{TiCl}_2$ (O-2,6- $\text{Pr}_2\text{C}_6\text{H}_3$ ) (**3a**) - MAO catalyst system. (ethylene 4 atm, styrene 5 mL, run 8, Table 2.)

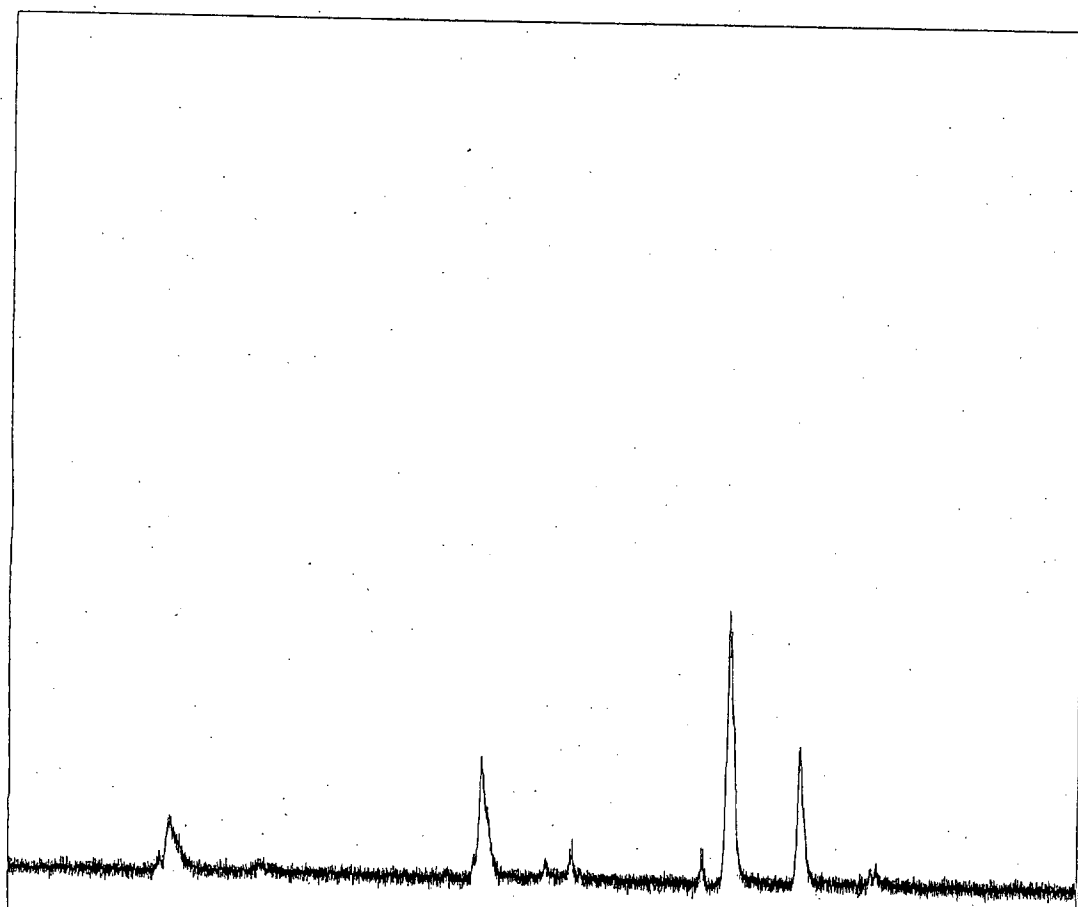


$^{13}\text{C}$  NMR spectrum for poly(ethylene *co*-styrene) (THF soluble fraction in  $\text{CDCl}_3$  at  $40^\circ\text{C}$ ) prepared by (1,3- $\text{Me}_2\text{C}_5\text{H}_3$ ) $\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$  (**3a**) MAO catalyst system. (ethylene 8 atm, styrene 5 mL, run 9, Table 2.)

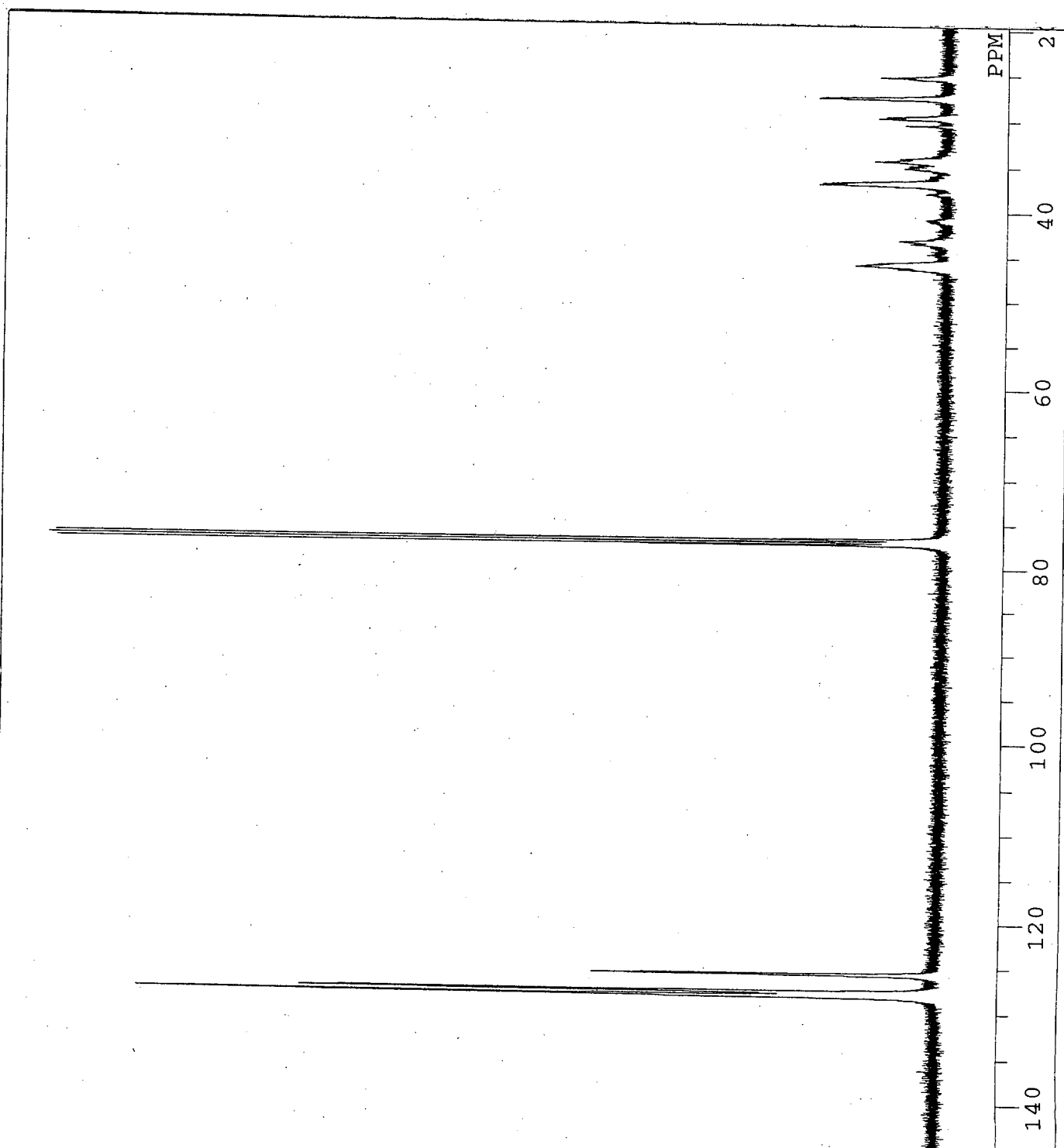


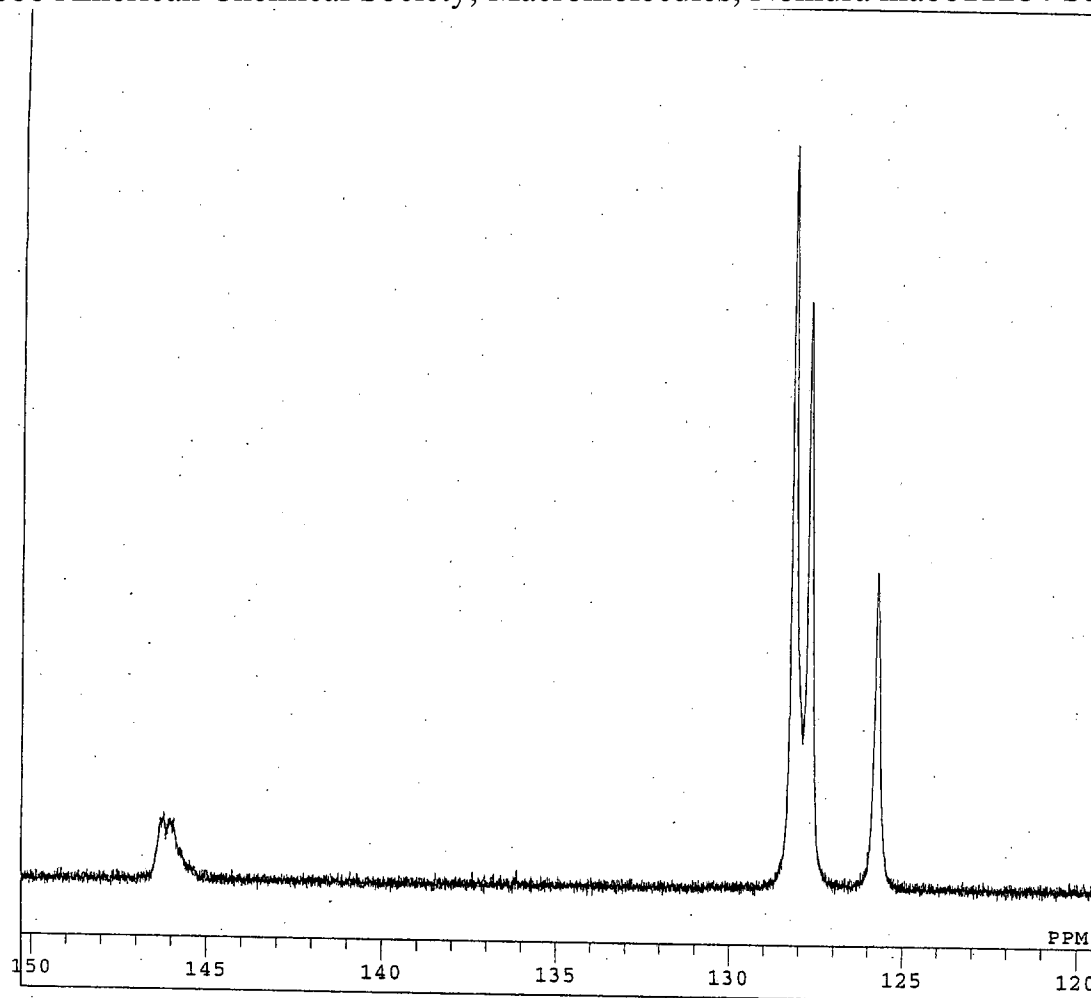


$^{13}\text{C}$  NMR spectrum for poly(ethylene-*co*-styrene) (THF soluble fraction in  $\text{CDCl}_3$  at 40 °C) prepared by (1,3- $\text{Me}_2\text{C}_5\text{H}_3$ ) $\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$  (**3a**) - MAO catalyst system. (ethylene 8 atm, styrene 5 mL, run 9, Table 2.)

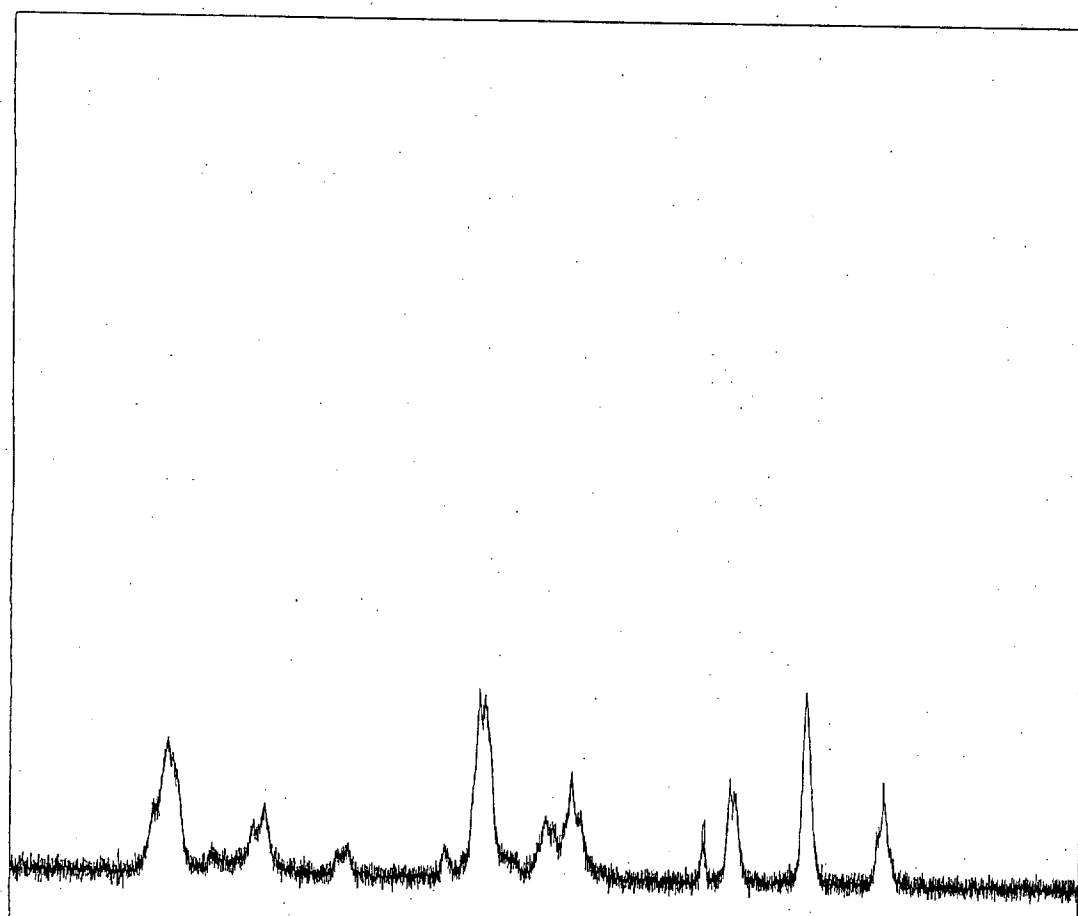


$^{13}\text{C}$  NMR spectrum for poly(ethylene-*co*-styrene) (THF soluble fraction in  $\text{CDCl}_3$  at  $60^\circ\text{C}$ ) prepared by (1,3- $\text{Me}_2\text{C}_5\text{H}_3$ ) $\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$  (**3a**) MAO catalyst system. (ethylene 3 atm, styrene 10 mL, run Table 2.)



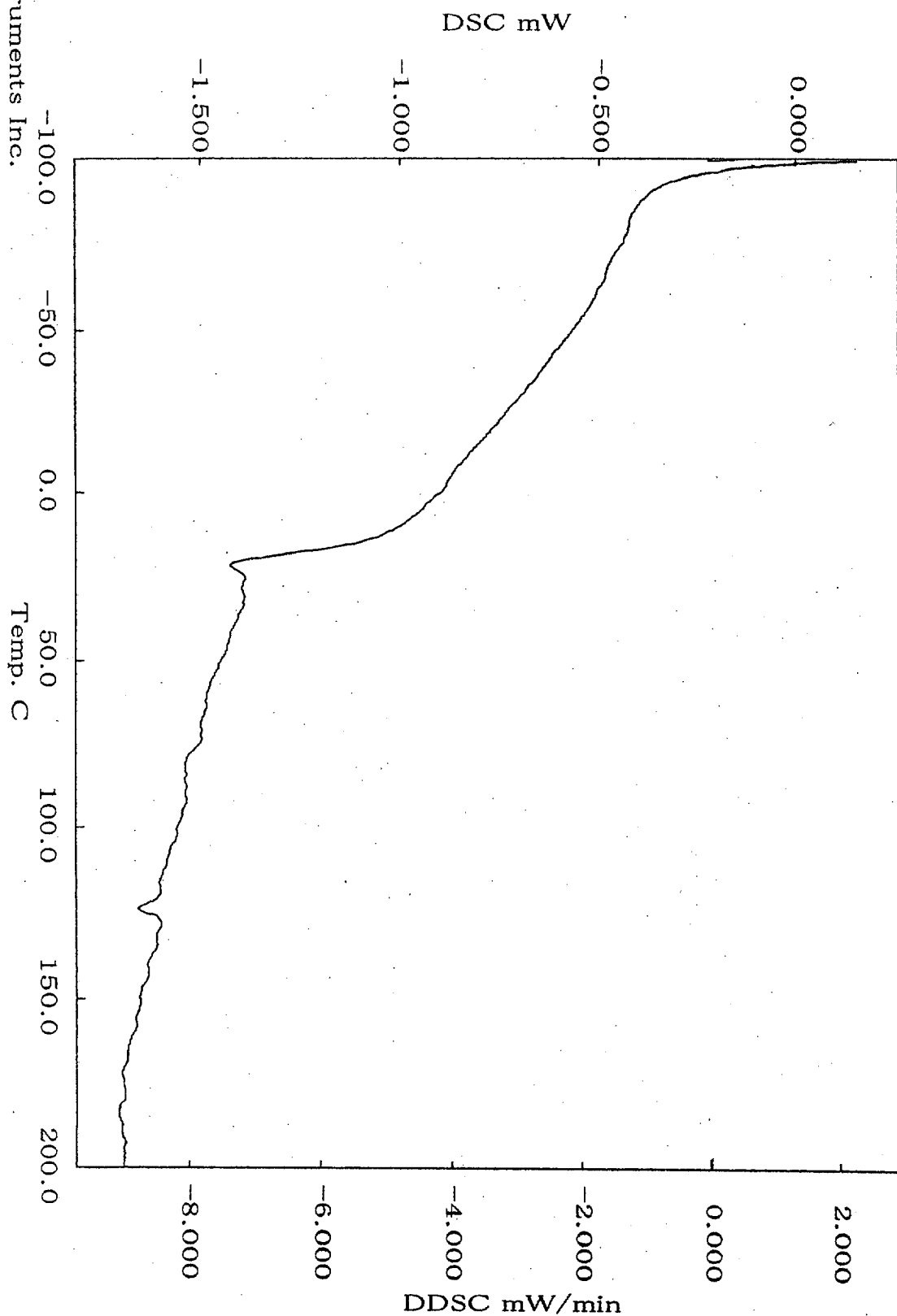


$^{13}\text{C}$  NMR spectrum for poly(ethylene-*co*-styrene) (THF soluble fraction in  $\text{CDCl}_3$  at  $60^\circ\text{C}$ ) prepared by (1,3- $\text{Me}_2\text{C}_5\text{H}_3$ ) $\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$  (**3a**) - MAO catalyst system. (ethylene 3 atm, styrene 10 mL, run 10, Table 2.)





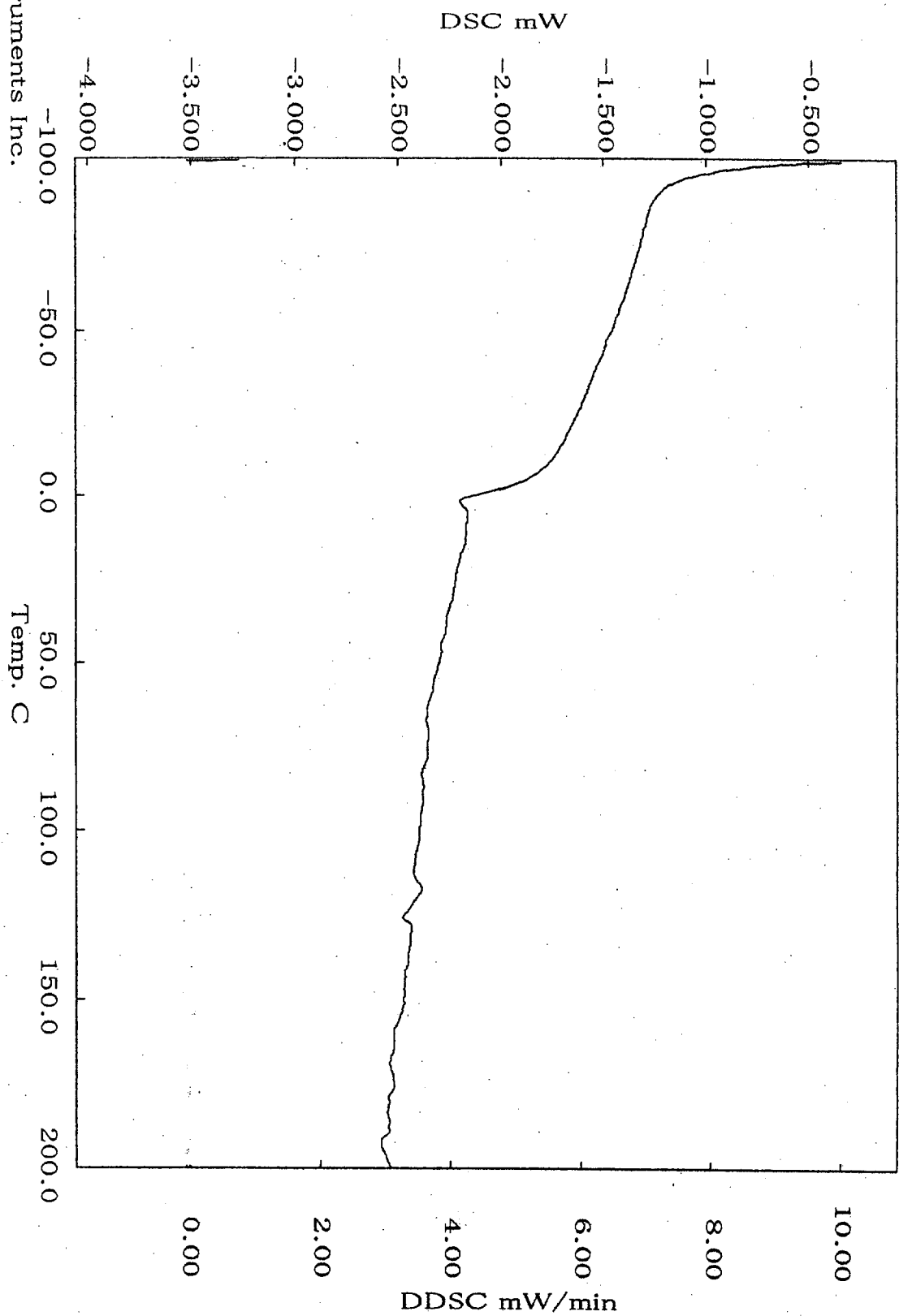
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4.9	3*	100 - 300	10	0	0.5
Al-empty pan	4	300 - 25	20	5	0.5
0					
	mg				



&lt;&lt; DSC &gt;&gt;

0/2/24 22:00					
E-S					
4.6	mg	1*	25 - 300	20	0
Al-empty pan	0	2	300 - -100	10	5
		3*	-100- 300	10	0
		4	300 - 25	20	5
					0.5

DSC trace for poly(ethylene-co-styrene  
(THF soluble fraction) prepared by  
(1,3-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>)TiCl<sub>2</sub>(O-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)  
(3a) - MAO catalyst system.  
(ethylene 8 atm, styrene 5 mL, run 9,  
Table 2.)



Seiko Instruments Inc.