Pressure Effects on Polymerization of Syndiotactic Polystyrene

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ABSTRACT: Polymerization pressure has a direct effect on the synthesis of syndiotactic polystyrene (*s*-PS) with metallocene as a catalyst. The polymerization rate, yield rate, and average molecular weight show a linear relationship with pressure, that is, they all increase with increased polymerization pressure. However, under 1000 psi, the yield of *s*-PS increases with polymerization duration while the yield rate decreases. As a whole, this syndiotactic polymerization proceeds relatively fast in comparison with ordinary vinyl polymerization. Optimal conditions (pressure, temperature, and duration) for the synthesis of *s*-PS have been explored. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1747–1752, 1998

Key words: polymerization pressure; syndiotactic polystyrene; metallocene

INTRODUCTION

Since Ishihara et al.^{1,2} adopted metallocene technology to synthesize syndiotactic polystyrene (s-PS), the latter has aroused wide attention and research interest due to its high syndiotacticity, high melting point, and high chemical stability. Recently, studies on polymerization conditions such as the molar ratio of the catalyst/cocatalyst and the reaction have been reported.^{1–5} However, another important variable-pressure-seems to have been neglected in those studies. From thermodynamic considerations, the increase in pressure favors the polymerization of polystyrene.⁶ This leads us to investigate pressure effects on styrene polymerization. The majority of highpressure studies reported in the literature were conducted in supercritical conditions, for exam-

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ple, ethylene to low-density polyethylene (LDPE). Thus, this work studied styrene polymerization with a metallocene catalyst under an inert argon gas ($T_c = -122.4$ °C, $P_c = 48$ atm) at various pressures from 1 to 100 atm to find the optimal conditions.

EXPERIMENTAL

Materials

Polymerization-grade styrene from Acros Co. was purified by being passed through a column of anhydrous Al_2O_3 before use. The metallocene catalyst (η -C₅H₅)TiCl₃ and the cocatalyst MAO were used without further purification.

Polymerization

The experiment was performed batchwise in a stirred autoclave. The autoclave reactor has a capacity of 300 mL and was designed for a maximum 5400 psi and temperature up to 300°C. It was equipped with a running agitator and a mag-

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Example	Molar Ratio Styrene:Al:Ti	Pressure N/m ² /[psi]	Temperature (°C)	Time (min)	Yield (g)	Insoluble in MEK (%)	M_w	T_m (°C)
1	$40,000:1000:1^{a}$	$6.893 imes 10^6$ /[1000]	40	60	30.82	73	155,441	253
2	$40,000:1000:1^{\mathrm{a}}$	$6.893 imes 10^6$ /[1000]	40	30	31.17	65	_	252
3	$40,000:1000:1^{\mathrm{a}}$	$6.893 imes 10^6$ /[1000]	40	20	26.45	70	_	252
4	$40,000:1000:1^{\mathrm{a}}$	$6.893 imes 10^6$ /[1000]	70	60	21.72	80	48,087	251
5	$40,000:1000:1^{\mathrm{a}}$	$6.893 imes 10^6$ /[1000]	70	30	18.41	75	41,211	253
6	$40,000:1000:1^{\mathrm{a}}$	$6.893 imes 10^6$ /[1000]	70	15	17.72	68	_	254
7	$40,000:1000:1^{\mathrm{a}}$	$6.893 imes 10^6$ /[1000]	70	10	16.81	62	_	252
8	$40,000:1000:1^{\mathrm{a}}$	$6.893 imes 10^6$ /[1000]	70	5	16.35	65	37,690	251
9	$40,000:1000:1^{\mathrm{a}}$	$1.034 imes 10^7$ /[1500]	70	60	26.93	76	52,522	252
10	$40,000:1000:1^{\mathrm{a}}$	$8.961 imes 10^6/[1300]$	70	60	24.67	78	49,601	250
11	$40,000:1000:1^{\mathrm{a}}$	$5.17 imes 10^{6}$ /[750]	70	60	25.10	61		250
12	$40,000:1000:1^{\mathrm{a}}$	$3.447 imes 10^{6}$ /[500]	70	60	24.8	60	_	254
13	$40,000:1000:1^{\mathrm{a}}$	$6.893 imes 10^6$ /[1000]	80	60	32.76	61	30,795	251
14	$40,000:1000:1^{\mathrm{a}}$	$6.893 imes 10^6$ /[1000]	90	60	8.93	63		251
15	$40,000:1000:1^{\mathrm{a}}$	$6.893 imes 10^6$ /[1000]	60	60	22.98	65	_	253
16	$40,000:2000:1^{ m b}$	$6.893 imes 10^6$ /[1000]	70	60	25.51	75		249
17	$40,000:500:1^{\circ}$	$6.893 imes 10^6$ /[1000]	70	60	34.5	50		252
18	$40,000:250:1^{ m d}$	$6.893 imes 10^6$ /[1000]	70	60	6.98	38	_	253
19	$40,000:250:1^{ m d}$	$6.893 imes 10^6$ /[1000]	70	240	12.17	33		253
20	$20,000:1000:1^{ m e}$	$6.893 imes 10^6$ /[1000]	70	60	48.9	85		251
Comparative 1	$40,000:1000:1^{\mathrm{a}}$	$1.013 imes 10^5$ /[14.7]	70	10	8.69	90	_	254
Comparative 2	$40,000:1000:1^{\mathrm{a}}$	$1.013 imes 10^5$ /[14.7]	70	60	10.75	89	—	254

Table I Results of s-PS Produced with Different Polymerization Conditions

^a Styrene = 100 g (0.96 mol); CpTiCl₃ = 2.4×10^{-5} mol in 4.7 mL of toluene; MAO = 2.4×10^{-2} mol in 16 mL of toluene. ^b Styrene = 100 g (0.96 mol); CpTiCl₃ = 2.4×10^{-5} mol in 4.7 mL of toluene; MAO = 4.8×10^{-2} mol in 32 mL of toluene. ^c Styrene = 100 g (0.96 mol); CpTiCl₃ = 2.4×10^{-5} mol in 4.7 mL of toluene; MAO = 1.2×10^{-2} mol in 8 mL of toluene. ^d Styrene = 100 g (0.96 mol); CpTiCl₃ = 2.4×10^{-5} mol in 4.7 mL of toluene; MAO = 6×10^{-3} mol in 4 mL of toluene. ^e Styrene = 100 g (0.96 mol); CpTiCl₃ = 4.8×10^{-5} mol in 4.7 mL of toluene; MAO = 4.8×10^{-2} mol in 16 mL of toluene.

net drive. To synthesize the syndiotactic polystyrene, the autoclave reactor was first degassed and filled up with Ar gas to replace the air. Subsequently, 100 g of styrene and 2.4×10^{-5} mol of CpTiCl₃ (dissolved in 4.7 mL of toluene) and 2.4 \times 10⁻² mol of methylaluminoxane (MAO) (dissolved in 16 mL of toluene) were introduced into the autoclave under an Ar atmosphere at the assigned temperature, for example, 40°C. The reaction pressure was adjusted to the assigned pressure, for example, 1000 psi, when the CpTiCl₃ was injected together with the MAO to start the polymerization. After 1 h, the pressure was released, and the polymerization reaction was stopped by the addition of acidified methanol. The resulting polymer was washed several times with 500 mL of methanol and vacuum-dried at 50°C for 24 h. The yield of polystyrene was 30.82 g, containing 73% of polystyrene with a syndiotacticity higher than 87%. The compound was extracted with boiling methyl ethyl ketone for 8 h, and the methyl ethyl ketone-insoluble polystyrene had a melting point of 253°C, a T_g of 99°C,

and a weight-average molecular weight of 155,441, with >99% syndiotacticity by ¹³C-NMR analysis. Experimental conditions and results are summarized in Table I.

Analysis

The molecular weight and the molecular weight distribution of the polymer were determined by GPC (Waters Model 150C) at 135°C using 1,2,4trichlorobenzene as a solvent or the mobile phase. This measurements were performed at the Chung Shan Institute of Science and Technology.

RESULTS AND DISCUSSION

The experimental data in Figure 1(a) indicate that the yield of *s*-PS linearly increases with the pressure of Ar (g) from 14.7 psi (1 atm) to 1500 psi (102 atm). Similarly, the polymerization rate increases with the pressure of Ar (g) as given in Figure 1(b). This behavior reveals that high pres-



Figure 1 Influence of polymerization pressure on *s*-PS yield and on the polymerization rate. Polymerization conditions: styrene = 0.96 mol, $\text{CpTiCl}_3 = 2.4 \times 10^{-5}$ mol in 4.7 mL of toluene, MAO = 2.4×10^{-2} mol in 16 mL of toluene, 70°C, 1 h.

sure favors the promoting of the syndiotactic insertion of the monomer unit in the polymerization process. This result is in good agreement with the thermodynamic prediction⁶ in which higher pressure favors the equilibrium from monomer to polymer. This syndiotactic polymerization is a very fast reaction under 1000 psi of Ar. An appreciable amount of *s*-PS shall be produced even during the first 5–10 min of the polymerization. The yield of *s*-PS is increases linearly with the duration of the polymerization during the first 60 min. However, the rate of *s*-PS produced decreases rapidly with the duration of polymerization as given



Figure 2 Influence of polymerization time on the polymerization rate under 1000 psia. Polymerization conditions: styrene = 0.96 mol, $\text{CpTiCl}_3 = 2.4 \times 10^{-5}$ mol in 4.7 mL of toluene, MAO = 2.4×10^{-2} mol in 16 mL of toluene, 70°C, 1000 psia.



Figure 3 Relation between polymerization pressure and weight-average molecular weight of s-PS. Polymerization conditions: styrene = 0.96 mol; CpTiCl₃ = 2.4 $\times 10^{-5}$ mol in 4.7 mL of toluene; MAO = 2.4 $\times 10^{-2}$ mol in 16 mL of toluene; 70°C, 1 h.

in Figure 2. This decreasing phenomenon is similar to those reported by Ishihara et al.²

The decrease may be attributed to the deactivation of the active centers or to the occlusion of part of the catalyst in the precipitating polymer. Similar results related to the rate of *s*-PS produced under 1 atm were reported by Ishihara et al.²

The effect of pressure from 1000 to 1500 psi on the molecular weight of *s*-PS at a 70°C polymerization temperature reveals a linear relationship as given in Figure 3. As the pressure increases, the molecular weight of *s*-PS increases. However, under a fixed 1000 psi, the molecular weight increases as the polymerization temperature decreases. The latter follows the general pattern of the free-radical polymerization. Figures 4 and 5 show the ¹³C-NMR spectrum of *s*-PS and of methylene carbon in *s*-PS.

CONCLUSION

The synthesis of *s*-PS under Ar gas at various pressures (14.7-1500 psi) has the following patterns:

- 1. Polymerization rate and yield of *s*-PS increase linearally with the pressure of Ar (g).
- 2. Under 1000 psi, the syndiotactic polymerization is a fast reaction with the





Figure 5 13 C-NMR spectrum of methylene carbon in *s*-PS.

yield of s-PS increasing linearly with the polymerization time during the first 60 min, while the rate of s-PS formation decreases rapidly with the duration of polymerization.

3. Under 1000 psi, the molecular weight of s-PS increases with increasing pressure while the polymerization temperature was 70°C and also decreases with increasing polymerization temperature. This research was supported by the National Science Council of the Republic of China (NSC 85-2214-E-007-006).

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