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Synthesis and thermal properties of poly(styrene-*co*-4-methylstyrene) produced with syndiospecific metallocene catalysts

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Poly(styrene-*co*-4-methylstyrene) with a different content of comonomer units was prepared using the typical syndiospecific homogeneous catalysts, i.e. η-$C_5H_5TiCl_3$ and η-$C_5(CH_3)_5TiCl_3$ combined with methylaluminoxane (MAO). The η-$C_5(CH_3)_5TiCl_3$ catalyst gave the polymers with higher syndiotacticity. The monomer reactivity ratios indicated that the copolymers obtained with η-$C_5H_5TiCl_3$ and η-$C_5(CH_3)_5TiCl_3$ possessed random and slightly blocky structure, respectively. With an increase in the 4-methylstyrene comonomer units, the glass transition temperature of the copolymer increased linearly and the crystallization temperature increased followed by a decrease in the melting point. © 1997 Elsevier Science Ltd.

(Keywords: metallocene catalysts; styrene-4-methylstyrene copolymer; thermal properties)

INTRODUCTION

The synthesis[1-4] of isotactic polystyrene (i-PolySt), as well as its fundamental properties such as crystallization[5], thermal properties[1,3] and mechanical properties[6] have been extensively studied since the pioneering work of Natta[1]. Although i-PolySt has a potential utility as a plastic with a high heat-resistance, the rate of crystallization is too slow to be practically applied. Recently, syndiotactic polystyrene (s-PolySt) has been prepared using the metallocene catalysts[7-9]. The s-PolySt is a crystalline polymer with a high melting temperature (about 540 K) and a high rate of crystallization. Numerous studies[7-21] have been made to investigate the molecular morphology of s-PolySt, like polymorphic properties, crystallization processes, crystal modification, etc. However, the properties of related copolymers have not yet been satisfactorily investigated. In particular, the effect of comonomer units in s-PolySt chain on the thermal properties has rarely been examined. As is well known, the thermal properties of polymers like melting, glass transition point (T_g) and crystallization temperatures are related to the chain stiffness, which is primarily affected by the barrier to rotation around backbone bonds. The barrier is controlled predominantly by the steric hindrance and intra-/intermolecular interactions which are caused by the bulkiness and polarity of the substituent groups. Thus, introduction of a comonomer into s-PolySt may have a potential to control the thermal properties of s-PolySt.

In this paper, we have synthesized poly(styrene-*co*-4-methylstyrene) with a different content of comonomer units, and examined the effects of a comonomer content on the glass transition point and melting temperatures as well as the crystallization behavior of s-PolySt.

EXPERIMENTAL

Materials

η-$C_5H_5TiCl_3$ commercially obtained from Aldrich Chemical Co. was used without further purification. Methylaluminoxane (MAO) was donated by Tosoh Akzo Chemical Co. η-$C_5(CH_3)_5TiCl_3$ was synthesized according to the literature[22]. Toluene, styrene and 4-methylstyrene were also commercially obtained from Nacalai Tesque Co. Toluene was dried over calcium hydride under reflux for 24 h, and distilled before use. Styrene and 4-methylstyrene were distilled over calcium hydride under reduced pressure before use.

Polymerization and polymer characterization

The polymerizations of styrene and 4-methylstyrene

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Table 1 Yields and molecular weights of copolymers obtained with η-$C_5H_5TiCl_3$/MAO and η-$C_5(CH_3)_5TiCl_3$/MAO

Metal compound	St content[a] (mol%)	Rate $\times 10^{-3}$ [b] (g polymer per g Ti)	$\bar{M}_n \times 10^{-3}$ [c]	$\bar{M}_w/\bar{M}_n$
η-$C_5H_5TiCl_3$	100	0.92	17	2.3
	89	1.10	17	2.7
	73	0.58	11	2.1
	49	1.28	17	2.3
	27	2.06	19	2.4
	0	2.49	20	2.5
η-$C_5(CH_3)_5TiCl_3$	100	0.31	42	1.8
	88	0.16	49	1.8
	77	0.19	55	2.0
	56	0.16	23	4.4
	30	0.21	17	4.6
	6	0.24	23	4.7
	0	1.05	31	5.1

[a] Determined by ^{1}H n.m.r.
[b] Polymerization conditions: monomer = 87 mmol; η-$C_5H_5TiCl_3$, η-$C_5(CH_3)_5TiCl_3$ = 0.015 mol; MAO = 4.5 mmol; toluene = 30 ml; polym. temp. = 50°C; polym. time = 2 h
[c] Estimated from g.p.c. (based on PolySt)

and the copolymerization of the two monomers were carried out at 50°C in a 100-ml glass reactor equipped with a magnetic stirrer under nitrogen atmosphere using toluene as the solvent. Polymerization was quenched by adding acidic methanol and the precipitated polymers were washed with acidic methanol, followed by drying in vacuum at 60°C. The polymers were then fractionated by exhaustive extraction with boiling methyl ethyl ketone in a soxhlet extractor.

The microstructure of polymers was determined by ^{1}H nuclear magnetic resonance (n.m.r.) and ^{13}C (n.m.r.). The 300 MJz ^{1}H n.m.r. and 75.5 MHz ^{13}C n.m.r. spectra were recorded on a Varian Gemini 300 spectrometer at 50°C in $CDCl_3$, or at 100°C in C_6D_6.

The molecular weight and molecular mass distribution of polymers were measured at 130°C by gel permeation chromatography (g.p.c.), with a Senshu Scientific SSC-7100 system using *o*-dichlorobenzene as the solvent.

Differential scanning calorimetry (d.s.c.) measurements were made with a Mettler DSC 820 under nitrogen atmosphere. Polymer samples (10–15 mg) were encapsulated in aluminium pans. All samples encapsulated in the aluminium pans were heated in d.s.c. equipment and kept at 563 K for 5 min. The samples were immediately quenched by immersing in a liquid nitrogen bath to obtain the noncrystalline glassy samples. The thermograms of samples thus obtained were measured at a heating rate of 20 K min^{-1}. The specific heat capacity, C_p, was evaluated using the C_p of α-Al_2O_3 (dried at 773 K) as reference.

RESULTS AND DISCUSSION

Preparation of samples

The results of homo- and copolymerization of styrene (St) and 4-methylstyrene (MSt) are given in *Table 1*. The yield of poly(4-methylstyrene) (s-PolyMSt) was slightly higher than that of s-PolySt for each catalyst, which can be explained in terms of the electron donating effect of the CH_3 substituent[16].

Figures 1 and *2* show the g.p.c. curves of s-PolySt, s-PolyMSt and s-Poly(St-*co*-MSt) obtained with the η-$C_5H_5TiCl_3$ and η-$C_5(CH_3)_5TiCl_3$ catalysts. The number-average molecular weights ($\bar{M}_n$) and polydispersities ($\bar{M}_w/\bar{M}_n$) of those polymers are summarized in *Table 1*. When the η-$C_5(CH_3)_5TiCl_3$ catalyst was employed, the molecular mass distribution of s-Poly(St-*co*-MSt) became broader with an increase in the MSt content, the reason of which is not clear at the moment.

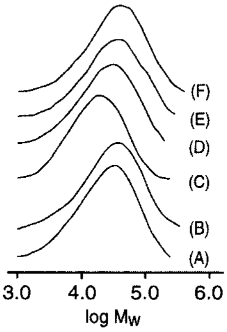

Figure 1 G.p.c. curves of polymers obtained with η-$C_5H_5TiCl_3$/MAO: (A) s-PolySt; (B) St/MSt, 89 mol% of St; (C) St/MSt, 73 mol% of St; (D) St/MSt, 49 mol% of St; (E) St/MSt, 27 mol% of St; (F) s-PolyMSt

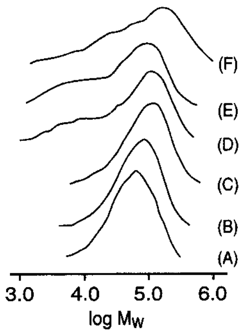

Figure 2 G.p.c. curves of polymers obtained with η-$C_5(CH_3)_5TiCl_3$/MAO: (A) s-PolySt; (B) St/MSt, 88 mol% of St; (C) St/MSt, 77 mol% of St; (D) St/MSt, 56 mol% of St; (E) St/MSt, 30 mol% of St; (F) s-PolyMSt

Figures 3–5 illustrate the ^{13}C n.m.r. spectra of s-PolySt, s-PolyMSt and s-Poly(St-*co*-MSt) obtained with the two catalyst systems. The peaks at around 145.4, 44.6 and 41.6 ppm in *Figure 3* can be assigned to the phenyl

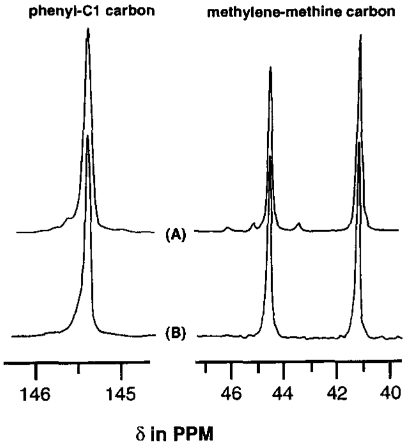

Figure 3 ^{13}C n.m.r. spectra of s-PolySt: (A) with η-$C_5H_5TiCl_3$/MAO; (B) with η-$C_5(CH_3)_5TiCl_3$/MAO, MEK insoluble fractions, TMS scale

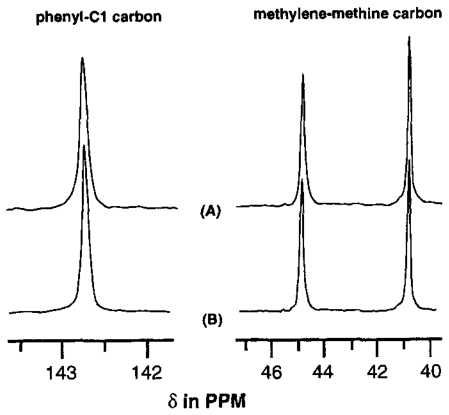

Figure 4 ^{13}C n.m.r. spectra of s-PolyMst: (A) with η-$C_5H_5TiCl_3$/MAO; (B) with η-$C_5(CH_3)_5TiCl_3$/MAO, MEK insoluble fractions, TMS scale

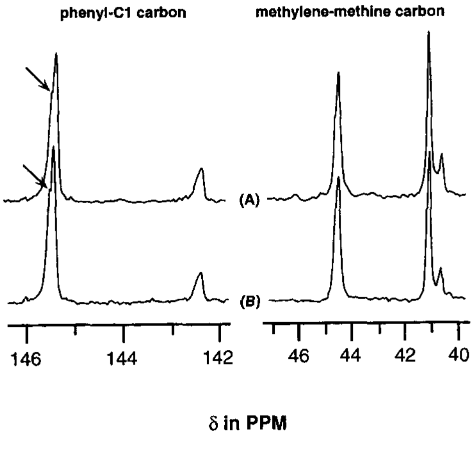

Figure 5 ^{13}C n.m.r. spectra of poly(St-*co*-MSt): (A) St/MSt, 73 mol% of St with η-$C_5H_5TiCl_3$/MAO; (B) St/MSt, 77 mol% of St with η-$C_5(CH_3)_5TiCl_3$/MAO, arrows indicate stereoirregular homosequences of St, MEK insoluble fractions, TMS scale

Cl, CH_2 and CH carbons of s-PolySt, respectively. The corresponding peaks appeared at 142.8, 44.8 and 41.8 ppm in the spectrum of s-PolyMSt (*Figure 4*). Such a shift of the phenyl Cl in s-PolyMSt may be due to an increase of shielding caused by the electron donating effect of the CH_3 group. The [rrrr] pentads were determined from the phenyl Cl peaks to obtain approximately 93% and 100% for polySt produced with the η-$C_5H_5TiCl_3$ and η-$C_5(CH_3)_5TiCl_3$ catalysts. These results indicate that the η-$C_5(CH_3)_5TiCl_3$ catalyst is more syndiospecific, while both the catalysts gave s-PolyMSt with [rrrr] $\cong$ 100%.

Zambelli *et al.*[13] have already investigated the structure of s-Poly(St-*co*-MSt) obtained with the tetrabenzyltitanium-MAO catalyst by ^{13}C n.m.r. They observed two peaks (at around 143.5 and 140.9 ppm, HMDS scale) corresponding to the phenyl Cl, which were broader as compared with s-Poly(St) and s-Poly (MSt). In *Figure 5* are illustrated the ^{13}C n.m.r. spectra of methyl ethyl ketone (MEK) insoluble fractions of typical s-Poly(St-*co*-MSt) obtained with the η-$C_5H_5TiCl_3$ and η-$C_5(CH_3)_5TiCl_3$ catalysts. In addition to the two peaks reported by Zambelli *et al.*, those spectra display a shoulder peak at around 145.6 ppm which can be assigned to stereoirregular homosequences of St. It may be considered, therefore, that these Poly(St-*co*-MSt) are cosyndiotactic polymers with a few steric defects.

The monomer reactivity ratio was then evaluated by means of the curve fitting method using the following Mayo–Lewis[23] equation,

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}\right) \qquad (1)$$

where $[M_1]$ and $[M_2]$ are the mole fractions of monomers in the feed and $d[M_1]/d[M_2]$ is the ratio of polymerization rates as determined from the yield and ^1H n.m.r. analysis of copolymer. The fitting results are shown in *Figure 6* together with the estimated r_1r_2 values, suggesting that

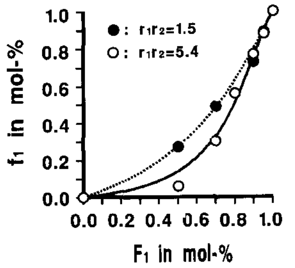

Figure 6 Mayo–Lewis plots for St-MSt copolymerization: M_1 = styrene and M_2 = 4-methylstyrene. ●, obtained with η-$C_5H_5TiCl_3$/MAO ($r_1 = 0.5$, $r_2 = 3$); ○, obtained with η-$C_5(CH_3)_5TiCl_3$/MAO ($r_1 = 0.6$, $r_2 = 9$)

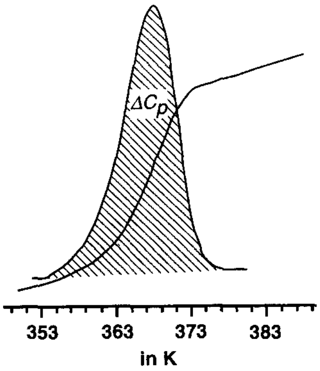

Figure 7 Dependence of specific heat capacity C_p and its derivative dC_p/dT of s-PolySt on temperature. The hatched portion represents ΔC_p

Table 2 T_g and ΔC_p of copolymers obtained with η-$C_5H_5TiCl_3$/MAO and η-$C_5(CH_3)_5TiCl$/MAO[a]

Metal compounds	St content (mol%)	T_g (K)	ΔC_p ($J\,g^{-1}K^{-1}$)
η-$C_5H_5TiCl_3$	100	367.9	0.19
	89	368.6	0.31
	73	366.6	0.32
	49	369.6	0.31
	27	378.3	0.32
	0	378.9	0.30
η-$C_5(CH_3)_5TiCl_3$	100	373.0	0.22
	88	373.3	0.35
	77	374.9	0.39
	56	376.3	0.35
	30	376.6	0.33
	6	380.2	0.38
	0	385.2	0.36

[a] Determined by d.s.c. (heating rate = 20 K min^{-1})

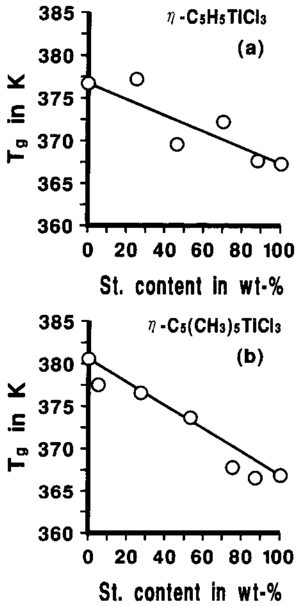

Figure 8 Modified T_g of poly(St-*co*-MSt) as a function of St content. The solid line represents the values calculated by the Fox equation. (a) With η-$C_5H_5TiCl_3$/MAO. (b) With η-$C_5(CH_3)_5TiCl_3$/MAO

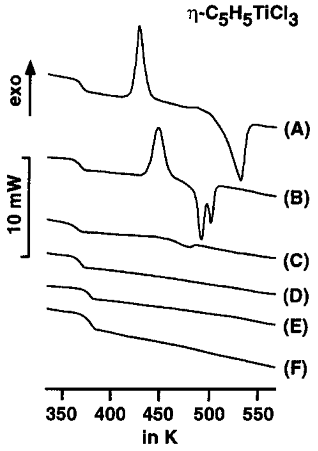

Figure 9 D.s.c. thermograms of polymers obtained with η-$C_5H_5TiCl_3$/MAO: Heating rate 20 K min^{-1}: (A) s-PolySt; (B) St/MSt, 89 mol% of St; (C) St/MSt, 73 mol% of St; (D) St/MSt, 49 mol% of St; (E) St/MSt, 27 mol% of St; (F) s-PolyMSt

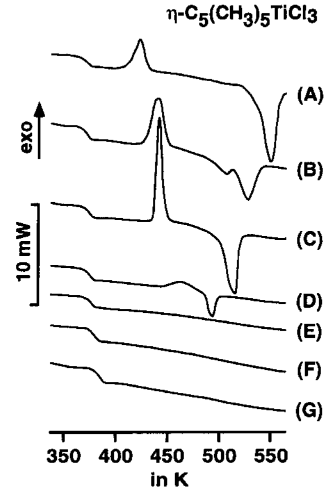

Figure 10 D.s.c. thermograms of polymers obtained with η-$C_5(CH_3)_5TiCl_3$/MAO: Heating rate 20 K min^{-1}: (A) s-PolySt; (B) St/MSt, 88 mol% of St; (C) St/MSt, 77 mol% of St; (D) St/MSt, 56 mol% of St; (E) St/MSt, 30 mol% of St; (F) St/MSt, 6 mol% of St; (G) s-PolyMSt

the copolymers obtained with η-$C_5H_5TiCl_3$ and η-$C_5(CH_3)_5TiCl_3$ catalysts possess random and slightly blocky structure, respectively.

Thermal properties of samples

As an example, in *Figure 7* are shown the temperature dependences of the specific heat capacity C_p and its derivative dC_p/dT of the s-PolySt obtained with the η-$C_5H_5TiCl_3$ catalyst. The specific heat is discontinuous and dC_p/dT displays a maximum in the region of glass transformation. The values of T_g and ΔC_p can be estimated from the peak position and the area (hatched portion in *Figure 7*) of the dC_p/dT vs T curve[24]. The values of T_g and ΔC_p are summarized in *Table 2*.

The T_g values of s-PolySt, s-PolyMSt and Poly(St-*co*-MSt) obtained with the η-$C_5H_5TiCl_3$ catalyst were found to be slightly lower as compared with those obtained with the η-$C_5(CH_3)_5TiCl_3$ catalyst. Since both the T_gs corrected by the following Flory equation[25] agree well

Table 3 Melting temperature, T_m and heat of fusion, ΔH, of copolymers[a]

St content[b] (mol%)	T_m (K)	ΔH (J g^{-1})	St content[c] (mol%)	T_m (K)	ΔH (J g^{-1})
100	531	19.6	100	549	32.5
89	503, 491	23.0	88	527, 507	22.9
73	480	1.1	77	514	26.6
49	–	–	56	493	5.2
27	–	–	30	–	–
0	–	–	6	–	–
–	–	–	0	–	–

[a] Determined by d.s.c. (heating rate 20 K min^{-1})
[b] η-$C_5H_5TiCl_3$/MAO
[c] η-$C_5(CH_3)_5TiCL_3$/MAO

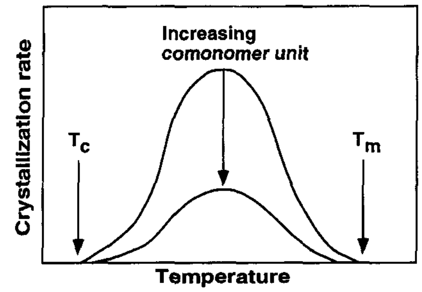

Figure 11 Crystallization curve as a function of crystallization temperature

with each other, such a difference in the apparent T_g may result from the difference in molecular weights.

$$T_g = T_g^{\infty} - 1.75 \times 10^5/\bar{M}_n \qquad (2)$$

In *Figures 8a* and *8b* are plotted the corrected T_gs of Poly(St-*co*-MSt), against the St content, where the solid lines represent the values calculated from the following Fox equation[26],

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (3)$$

where w_i and T_{gi} denote the weight fraction in copolymer and T_g of homopolymer, respectively. The T_g increased linearly with an increase in the content of MSt. A scattering around equation (3) is observed as seen in *Figure 8a*. This scattering may be associated with poor stereoregularity of polymers since the stereoregularity of the polymer produced with η-$C_5H_5TiCl_3$ is lower than that obtained with η-$C_5(CH_3)_5TiCl_3$ as mentioned above. The effect of a chain length on T_g is closely related to the intermolecular forces, i.e. chain stiffness and stereoregularity. The higher T_g of s-PolyMSt as compared with that of s-PolySt is responsible for the hindrance of free rotation along the polymer chain, which is caused by the bulky CH_3 group as well as the intermolecular forces quantified by the cohesive energy.

With both catalyst systems, s-PolySt showed a smaller ΔC_p as compared with those of s-PolyMSt and Poly(St-*co*-MSt). The ΔC_p value is known to depend markedly on the chain stiffness, because it is directly related to the conformational entropy in the glassy state. According to the Raman spectrometry reported by Kobayashi *et al.*[15], the chain stiffness of s-PolySt is much greater than those of a-PolySt and i-PolySt. Therefore, such large ΔC_ps values observed in the present copolymers seem to be associated with a high flexibility of the backbone chain, which probably results from a poor syndiotacticity.

The d.s.c. thermograms of melting and crystallization of both homopolymers and copolymers are shown in *Figures 9* and *10*, while, the melting temperature, T_m, and the heat of fusion, ΔH, are summarized in *Table 3*.

The s-PolySt displayed a crystallization (endothermic) peak, T_c, as well as a melting (exothermic) peak, T_m. However, the corresponding peaks disappeared with an increase in the MSt content. It was confirmed by the wide angle X-ray analysis that s-PolyMSt is a noncrystalline polymer. It is likely that the bulkiness or the electron donating effect of the CH_3 group may prevent the s-PolySt from crystallization. As a result, it is likely that the incorporation of the CH_3 group leads to a depressed bell-shaped crystallization–temperature curve, as schematically shown in *Figure 11*, and consequently causes an increase of T_c and a decrease of T_m, e.g. the T_m of copolymer containing 11% MSt with η-$C_5H_5TiCl_3$/MAO is 28 K lower than that of s-PolySt (531 K) and the T_c of that is 21 K higher than that of s-PolySt (427 K). *Figures 9* and *10* indicate that the copolymers containing about 10% MSt display double melting peaks, i.e. T_m = 503 and 491 K for η-$C_5H_5TiCl_3$/MAO and T_m = 527 and 507 K for η-$C_5(CH_3)_5TiCl_3$/MAO, which were converted to a single melting peak by the isothermal heat treatment. The double melting peaks can be ascribed to the modification of crystal form[20] and/or a partial inclusion of comonomer units in the crystals[27].

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