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Preparation and characterization of hydrogenated syndiotactic polystyrene

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Abstract

Syndiotactic polystyrenes (sPS) with different molecular weights were hydrogenated over the Ni/SiO_2 and $Pd\text{-}BaSO_4$ catalysts. Although the Ni catalyst yielded a completely hydrogenated sPS with a lower molecular weight, the hydrogenation of sPS with a high molecular weight was incomplete. On the other hand, the Pd catalyst was capable of hydrogenating sPS with a high molecular weight. However, the hydrogenated sPS (HsPS) was found to contained a small quantity of isolated styrene units. From a detailed analysis of the HsPS by differential scanning calorimetry (d.s.c.) and X-ray, it was revealed that this HsPS has a potential as a crystalline material with an excellent heat-resistance.

Keywords: Syndiotactic polystyrene; Hydrogenation; Semi-crystalline polymer

1. Introduction

The hydrogenation technique is a powerful tool for the preparation of model polymeric materials with controlled microstructures [1–4]. This technique has been often utilized to saturate the aromatic ring in atactic or isotactic polystyrene. As compared to polystyrene, the hydrogenate polystyrene, i.e., poly(vinyl cyclohexane) (PVCH), shows a higher glass transition temperature [5,6] and a lower density [7]. We have previously prepared a syndiotactic PVCH with a lower molecular weight ($\bar{M}_n \cong 3 \times 10^3$) using the hydrogenation technique [8]. However, the physical properties of the resulting polymer have not been investigated satisfactorily because of the insufficient molecular weight.

In this work, the method was successfully applied to the hydrogenation of a higher molecular weight syndiotactic polystyrene (sPS) and, thus, the thermal properties and crystallizability of the hydrogenated sPS were investigated in some detail.

2. Experimental

2.1. Materials

Styrene commercially obtained from Nacalai Tesque Co. was washed with an aqueous solution of sodium hydroxide, dried over calcium hydride for 24 h, and distilled under reduced pressure before use. Toluene used as the solvent was purified by refluxing over calcium hydride for 24 h, followed by fractional distillation. Methylaluminoxane (MAO) was prepared from $AlMe_3$ and $CuSO_4 \cdot 5H_2O$ according to the literature [9] and reserved as a stock solution in toluene, 1.04 mol/l. The $AlMe_3$ and $CuSO_4 \cdot 5H_2O$ commercially obtained from Tosoh Akzo Chemical Co. and Nacalai Tesque Co., were used without further purification. $\eta\text{-}C_5H_5TiCl_3$ was commercially obtained from Aldrich Chemical Co. and used without further purification. $\eta\text{-}C_5(CH_3)_5TiCl_3$ was synthesized according to the literature [10]. The silica-supported Ni catalyst ($Ni(10\ wt\%)/SiO_2$) was prepared by contacting the silica gel with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$, followed by filtration and drying at 573 K for 2 h. Prior to the hydrogenation reaction, the Ni/SiO_2 catalyst was reduced at 573 K for 2 h under a H_2 atmosphere. The $Pd(5\ wt\%)\text{–}BaSO_4$ catalyst commercially obtained from Aldrich Chemical Co. was used without further treatment. Methylcyclohexane obtained from Nacalai Tesque Co. was distilled over calcium hydride before use.

For the synthesis of a low-molecular weight syndiotactic polystyrene (sPS: $\bar{M}_n \cong 3 \times 10^4$), polymerization was conducted at 303 K for 24 h in a stirred 100 ml glass reactor under nitrogen by using toluene (30 ml), $\eta\text{-}C_5H_5TiCl_3$ (0.015 mmol), MAO (6.7 mmol) and styrene (87 mmol). Whereas the sPS with a higher molecular weight ($\bar{M}_n \cong 2 \times 10^5$) was prepared from a polymerization

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conducted at 343 K for 24 h in a stirred 100 ml glass reactor using η-$C_5(CH_3)_5TiCl_3$ (0.03 mmol), MAO (13.5 mmol) and styrene (174 mmol) in the absence of toluene solvent.

All the polymerizations were quenched by adding acidic methanol. The precipitated polymers were dried under reduced pressure at 333 K. The polymers were fractionated by exhaustive extraction with boiling methyl ethyl ketone in a Soxhlet extractor. The resulting samples were then dissolved in boiling xylene to make a 1% solution at 403 K and successively filtered in order to separate the catalyst. The filtrate was reprecipitated in a 15-fold excess of methanol and dried in a vacuum oven at 393 K for 40 h. The glassy films of sPS were prepared as follows: the purified sPS sample was pressed at 563 K under 10 MPa for 6 min and immediately quenched into an ice-water bath.

2.2. Hydrogenation reaction

The hydrogenation reaction of sPS was performed under 12 MPa of hydrogen for 72 h at 463 K in a stirred 100 ml stainless steal reactor, using a glassy sPS film (1 g), methylcyclohexane (40 ml) and the Ni/SiO_2 or Pd(5 wt%)–$BaSO_4$ catalyst (0.1 g). The resulting polymer was dissolved in boiling xylene to make a 1 % solution and successively filtered to remove the catalyst. The filtrate was reprecipitated in a 15-fold excess of methanol containing a small amount of BHT (3,5-di-*t*-butyl-4-hydroxytoluene) as an antioxidant, and the powdery sample thus obtained was dried in a vacuum oven at 403 K for 40 h. The recovery of samples, namely, the weight fraction of boiling xylene-soluble part was about 100 wt%, with the exception of the sample prepared by using the Pd-$BaSO_4$ catalyst. The recovery of this sample was 43 wt%. The powdery sample was pressed at 463 K under 10 MPa for 8 min and immediately quenched into an ice-water bath.

2.3. Measurements

The molecular weight and molar mass distribution of polymers were determined by a high-temperature gel permeation chromatography instrument (Senshu Scientific SSC-7100) at 403 K using *o*-dichlorobenzene as the solvent.

The degree of hydrogenation was determined from ^1H nuclear magnetic resonance (n.m.r.) spectra. The 300 MHz ^1H n.m.r. spectra were recorded on a Varian Gemini 300 spectrometer at 313 K on 10% (w/v) solutions in $CDCl_3$. The existence of a cyclohexane ring was confirmed by ^{13}C n.m.r. measurements at 373 K on 10% (w/v) solutions in 1,2,4-trichlorobenzene/C_6D_6 (9/1, v/v) The CH and CH_2 subspectra were obtained by using the distortionless enhancement by polarization transfer (d.e.p.t.) pulse sequences. Fourier transformation infrared (FT-i.r.) spectra were recorded on a Jaso FT-IR 500 spectrometer at a resolution of 2 cm^{-1}. Differential scanning calorimetry (d.s.c.) measurements were made with a Mettler DSC 820. The sample of about 10 mg weight was sealed in an aluminium pan. The d.s.c. measurements of the samples were carried out at a heating rate of 20 K/min under a N_2 atmosphere. The decomposition of polymers was measured by a Mettler TGA80 thermogravimetry analyzer at a heating rate of 10 K/min under a N_2 atmosphere. The sample of about 10 mg weight was poured into an alumina crucible.

Table 1
Characteristic of the hydrogenated syndiotactic polystyrene

Run	Cat.	sPS sample	Degree of hydrenation (mol%)	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
1[a]	Ni/SiO_2	sPS[b]	≈ 100	0.3	2.8
2	Ni/SiO_2	sPS(l)[b]	54	3.4	2.2
3	Ni/SiO_2	sPS(h)[b]	0	—	—
4	$Pd/BaSO_4$	sPS(h)[b]	≈ 97	11.9	3.7

[a]From our previous data (Ref. [8])
[b]The letters l and h in parentheses indicate low and high molecular weights. sPS, $\bar{M}_n = 0.4 \times 10^{-4}$, $\bar{M}_w/\bar{M}_n = 3.0$; sPS(l), $\bar{M}_n = 3.0 \times 10^{-4}$, $\bar{M}_w/\bar{M}_n = 2.5$; sPS(h), $\bar{M}_n = 20.0 \times 10^{-4}$, $\bar{M}_w/\bar{M}_n = 2.6$.

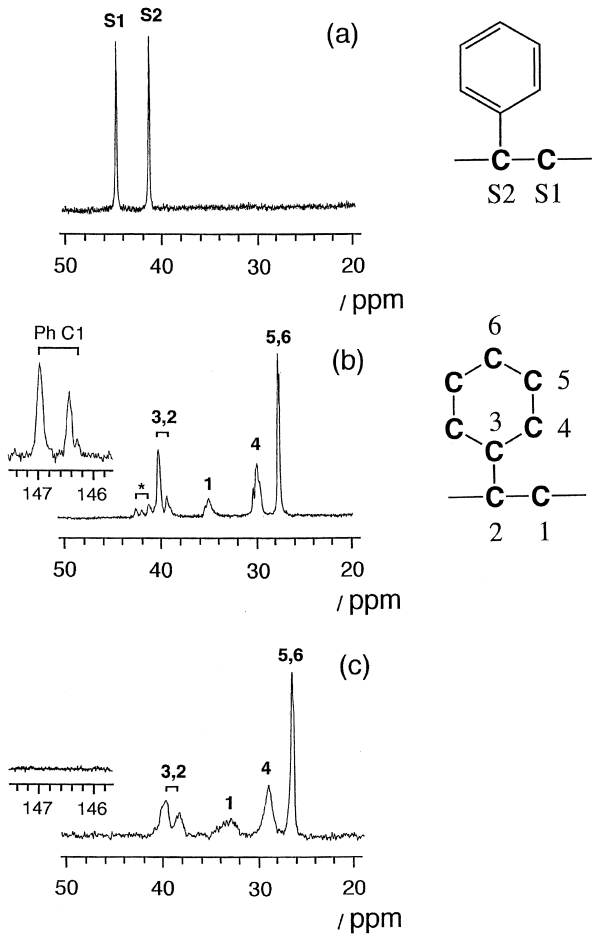

Fig. 1. ^{13}C n.m.r. spectra of polymer samples. (a) Syndiotactic polystyrene (sPS), (b) hydrogenated syndiotactic polystyrene (HsPS), (c) hydrogenated atactic polystyrene (HaPS); asterisk indicates the resonances resulting from isolated styrene unit and neighbouring vinyl cyclohexane units.

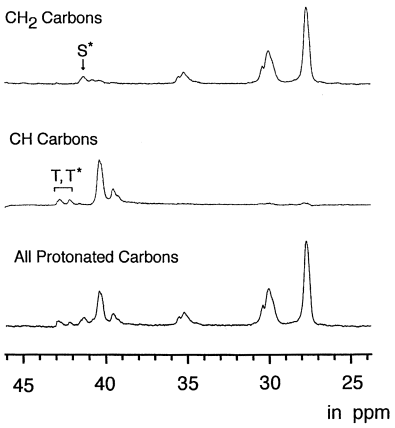

Fig. 2. ^{13}C n.m.r. d.e.p.t. spectra of HsPS sample.

The wide-angle X-ray diffractograms were recorded in reflection geometry at 1° (2θ/min) under Ni-filtered Cu Kα radiation using a Rigaku XG-RINT diffractometer.

3. Results and discussion

3.1. Sample preparation

Table 1 shows the degree of hydrogenation for the hydrogenated syndiotactic polystyrenes (HsPS) prepared by using the Ni/SiO_2 and $Pd\text{-}BaSO_4$ catalysts. The two catalysts employed here displayed totally different catalytic performance for the hydrogenation, the reason for which is, however, not obvious at present. For the complete hydrogenation of the higher-molecular weight sPS, the Ni/SiO_2 catalyst was not so effective. When the Pd catalyst was used, on the other hand, even the high-molecular weight sPS could be successfully hydrogenated. the boiling xylene-soluble fraction of the hydrogenated sPS (HsPS) was 43 wt%. The degree of hydrogenation in this fraction was about 97 mol%. It is known that a high-molecular weight isotactic PVCH is not soluble in boiling aromatic solvents [11]. Accordingly, the boiling xylene-insoluble fraction of the present HsPS might be a highly hydrogenated sPS, although it could not be demonstrated due to the difficulty of a detailed analysis. In the following, the xylene-soluble HsPS with a degree of hydrogenation of 97% was examined with regard to structure and properties.

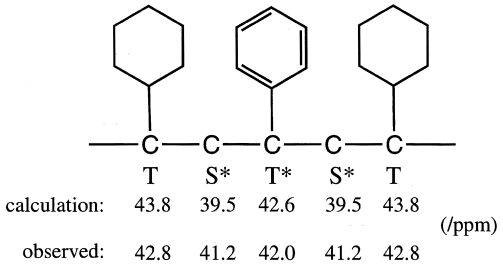

Fig. 3. Calculated ^{13}C chemical shifts of carbons of isolated styrene unit and of neighbouring vinyl cyclohexane units.

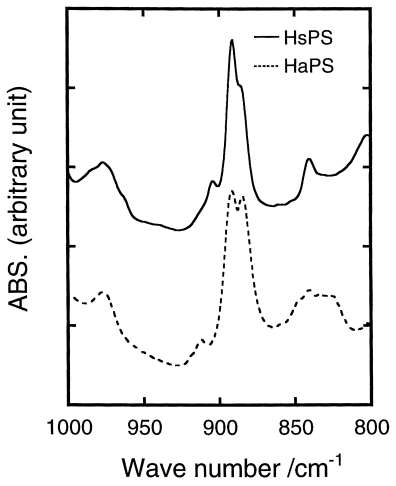

Fig. 4. Infrared spectra of HsPS and HaPS; solid line HsPS; broken line HaPS.

Fig. 1a and Fig. 1b illustrate the ^{13}C n.m.r. spectra of sPS and HsPS samples. For comparison, the ^{13}C n.m.r. spectrum of the completely hydrogenated atactic polystyrene (HaPS) sample is presented in Fig. 1c. The assignment of each resonance was made according to the literature [8,12]. The spectrum of HsPS (Fig. 1b) apparently displays some minor resonances in the region of 41-43 ppm. In order to make these minor resonances clear, we have employed the d.e.p.t. technique with two carbon types: CH and CH_2. As shown in Fig. 2, the CH_2 carbon (*S**, 41.2 ppm) resonates upfield from the CH carbons (*T*, 42.8 ppm; *T**, 42.0 ppm), indicating that these minor resonances are not ascribed to the CH and CH_2 carbons in styrene sequences [13]. Whereas the chemical shift of the minor resonances agree fairly with those of the carbons (calculated from Lindeman and Adams' rule [14,15]) in a sequence containing an isolated styrene unit as illustrated in Fig. 3.

The FT-i.r. spectra of HsPS and HaPS are shown in Fig. 4. The spectrum of HaPS displays doublet peaks at 890 and 885 cm^{-1} which are characteristic to atactic PVCH [6]. In

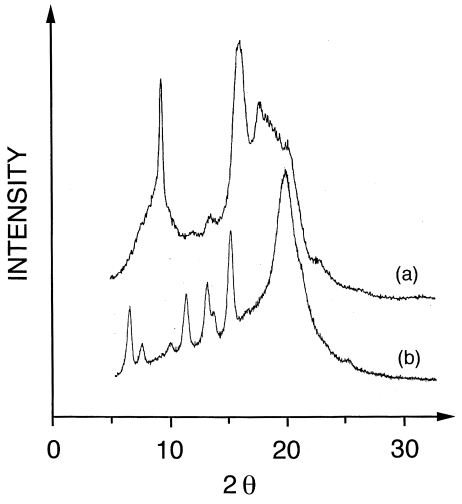

Fig. 5. X-ray diffraction pattern of slowly cooled films: (a) HsPS, (b) sPS.

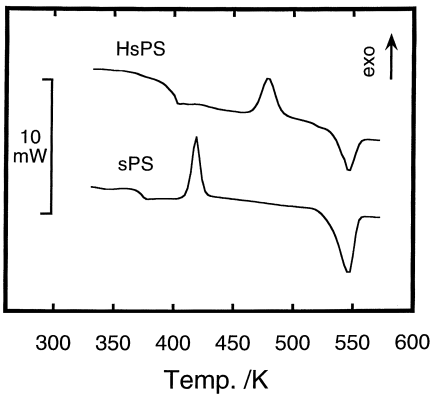

Fig. 6. The d.s.c. curves of HsPS and HaPS.

Table 2
Thermal properties of hydrogenated and original sPS

Sample	T_g^a (K)	T_c^b (K)	T_m^c (K)	ΔH_m^d (J g^{-1})
sPS	373	418	546	30
HsPS	399	479	546	17

[a]Glass transition temperature
[b]Crystallization temperature
[c]Melting temperature
[d]Heat of fusion

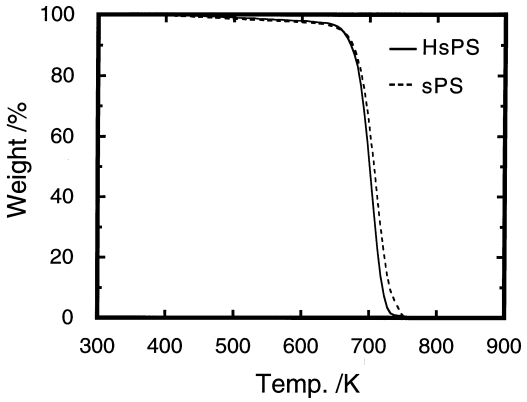

Fig. 7. The thermogravimetric (t.g.) curves of HsPS and sPS: solid line, HsPS; broken line, sPS.

the spectrum of HsPS, on the other hand, the intensity of the peak at 885 cm^{-1} seems to decrease to some extent, which may reflect a slight difference in the chain conformations between HaPS and HsPS.

4. Sample characterization

A HsPS was prepared by slowly cooling (− 2 K/min) the HsPS samples from 563 K down to the glass transition temperature (about 403 K) in the hot press. The film was analysed using wide-angle X-ray diffractograms (Fig. 5), which suggests the HsPS has a crystalline structure. Then, d.s.c. measurements were made on the quenched sPS and sPVCH films at a heating rate of 20 K/min (Fig. 6). The HsPS displays a crystallization (exothermic) peak T_c at 479 K and a melting (endothermic) peak T_m at 546 K. Some thermal properties of sPS and HsPS are compared in Table 2.

Finally, we have measured the decomposition temperature of the HsPS, the thermogravimetric (t.g.) curve of which is shown in Fig. 7 together with that of the sPS for reference. It was thus found that the decomposition temperatures of the HsPS and the original sPS are 704 and 709 K, respectively.

The results described in this paper suggest that the hydrogenated syndiotactic polystyrene (HsPS) could be applied as an excellent heat-resistance material.

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