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Syndiospecific copolymerization of styrene with styrene macromonomer bearing terminal styryl group by $CpTiCl_3$–methylaluminoxane catalyst

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Abstract

Copolymerization of styrene with styrene-terminated polystyrene macromonomer (SSTM) by $CpTiCl_3$–methylaluminoxane (MAO) catalyst was investigated. SSTM was prepared by a reaction of living polystyrene initiated with *sec*-butyllithium (*s*-BuLi) and *p*-chloromethyl styrene at −78°C. The synthesized SSTM has a high terminal functionality and a narrow molecular weight distribution. Graft copolymers of polystyrene consisted of syndiotactic main chain and atactic side chain were synthesized by $CpTiCl_3$–MAO catalyst. The synthesized graft copolymer was confirmed to have highly syndiotactic sequence on the main chain. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Syndiotactic graft copolymer; Styrene macromonometer; Metallocene catalyst

1. Introduction

Metallocene polymerizations of olefins is one of the excellent process for synthesizing stereoregular polymers. Ishihara et al. [1] first succeeded in preparing highly syndiotactic polystyrene (SPS) with half titanocene catalysts. After that, many works on the syndiospecific polymerization of styrene (St) and its derivatives have been reported with Ti-based metallocene catalysts [2]. Since SPS has superior physical properties such as a high melting temperature and a fast rate of the crystallization, the modification of SPS is interesting from the point of broadening the physical properties. One modification method of SPS for the physical properties is a synthesis of graft copolymers containing syndiotactic sequence of St units on the main chain.

Well-defined graft copolymers can be synthesized by macromonomer method through free radical polymerizations [3]. So far as using radical polymerization process, it is difficult to synthesize graft copolymers having stereoregularity on the main chain.

The stereoregular polymers can be synthesized with metallocene catalysts. Moreover, long chain monomers are possible to be incorporated in the polymers in the polymerization with some metallocene catalysts [4]. Thus, metallocene polymerizations are likely to be useful methods to make well-defined stereoregular graft copolymer on the main chain. Many types of graft copolymers such as polyethylene-*graft*-poly(St), polyethylene-*graft*-poly(*p*-methyl styrene) [5], polyethylene-*graft*-polypropylene [6] and polypropylene-*graft*-poly(St) [7] were synthesized with metallocene catalysts.

In a previous paper [8], we reported the synthesis of syndiotactic graft copolymers of SPS-*graft*-poly(IP). In this graft copolymer, each segment, i.e. poly(St) and poly(IP), is the immiscible. The styrene-terminated polystyrene macromonomer (SSTM) prepared through a living anionic polymerization is used as a branch segment, the graft copolymer consist of SPS-*graft*-atactic poly(St) (APS) and both segments are miscible. Hence the thermal behavior of the graft copolymer of SPS-*graft*-APS should be different from that of the syndiotactic poly(St)-*graft*-poly(IP). Since SSTM can be obtained from a reaction of a living polystyrene initiated with alkyllithiums and terminated with *p*-chloromethyl styrene (PCMS) [9], well-defined syndiotactic graft copolymers of SPS-*graft*-APS with controlled side chain length and number of the chain can be synthesized.

In this article, we will describe the synthesis of SSTM and syndiotactic copolymerization of SSTM with St by $CpTiCl_3$/MAO catalyst. The thermal behavior of the graft copolymer are also discussed.

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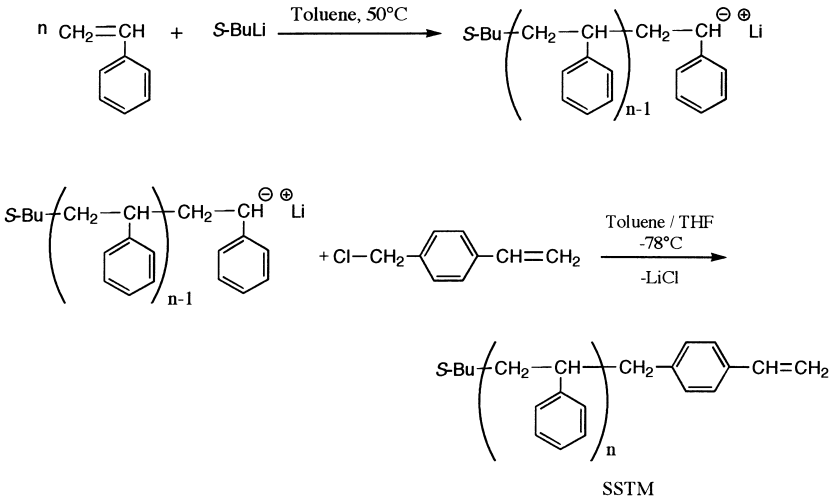

Scheme 1.

2. Experimental

2.1. Materials

Commercial grade St, and *p*-chloromethyl styrene (*p*-CMS) were purified by distillation before use. *sec*-Butyllithium (*s*-BuLi) diluted with cyclohexane was purchased from Kanto Chemical Co., and used as received. $CpTiCl_3$ (Aldrich Chem. Co.) were used without further purification. Methylaluminoxane (MAO) diluted with toluene kindly supplied from Tosoh-Akzo Chem. Co. was used as received. Solvents and other reagents were purified by conventional methods.

2.2. Synthesis of SSTM

The synthesis of SSTM was performed in a Taiatsu Glass Co. TEM-300 type glass reactor. The charging of the required amount of reagents was performed with syringes through a septum. A living polystyrene was prepared by the polymerization of St (1 mol/dm^{-3}) with *s*-BuLi (0.1 mol/dm^{-3}) in toluene at 50°C for 3 h. Then, the SSTM can be obtained from the reaction of the living polystyrene with *p*-CMS at *p*-CMS/Li mole ratio of 1.2 in the mixture of toluene/THF (9/1 v/v%) at −78°C for 12 h. After the reaction, the reaction products were poured in a large amount of methanol to precipitate SSTM, and dried in a vacuum. The yield was determined by gravimetry.

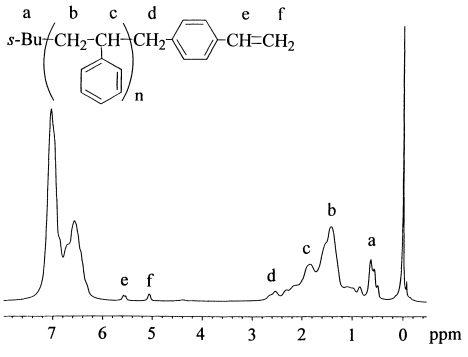

Fig. 1. ^{1}H NMR spectrum of SSTM.

2.3. Copolymerization of SSTM and St

Copolymerization of St with SSTM was carried out in the glass tube in toluene at 50°C. After the copolymerization the contents in the tube were poured into a large amount of methanol containing a small amount of hydrochloric acid to precipitate the graft copolymer, filtered off, washed with a large amount of methanol and dried in a vacuum. The graft polymer was extracted by methylethylketone (MEK), and the MEK-insoluble fraction was used as an index of syndiotacticity of the graft copolymer.

2.4. Characterization of polymers

The polymer structure was determined by NMR spectroscopy. ^{1}H and ^{13}C NMR spectra of the polymers were taken using JEOL A-400 spectrometer. Number average molecular weights of SSTM were determined by using vapor pressure osmometry (VPO) using Knauer Vapor Pressure Osmometer. The molecular weight distribution (M_w/M_n) of the polymer was estimated by GPC using Tosoh GPC-8000 series at 38°C in THF as calibrated with standards polystyrenes. The M_n of MEK-insoluble fraction and its M_w/M_n were determined by GPC using Waters 150C at 120°C in 1,2,4-trichlorobenzene. Thermal behavior of the polymers was investigated by differential scanning calorimeter (DSC) using SEIKO, S II EXSTAR 6000 thermal analyzer at heating rates of 10°C/min.

Table 1
Graft copolymerization of SSTM and St with $CpTiCl_3$–MAO catalysts in toluene at 50°C for 3 h ([St] = 2.9 mol/l, [Ti] = 4.7×10^{-4} mol/l, MAO/Ti = 500 mole ratio)

[SSTM][a] (g)	(Wt%)	Yield (%)[b]	MEK-insoluble (%) (Wt%)	($M_n \times 10^{-4}$)	(M_w/M_n)	SSTM content (mol %)	No. of SSTM (per chain)	Melting point (°C)
0.5	14.3	25.5	29.4	3.20	1.67	13.4	3.9	231.8
0.8	21.1	28.1	23.7	4.64	1.53	30.6	12.9	[c]

[a] [SSTM]; $M_n = 1100$, $M_w/M_n = 1.13$, $f = 0.98$.
[b] Include SSTM.
[c] No melting point was observed.

3. Results and discussions

3.1. Synthesis of SSTM

The SSTM was synthesized by the reaction of *p*-CMS with the living poly(St) obtained with *s*-BuLi catalyst in toluene at 50°C for 3 h according to Scheme 1. The mixed solvent of toluene and THF for this reaction was used to obtain high terminal functionality [4].

The molecular weight and polydispersities (M_w/M_n) of the SSTM were well controlled similarly to those prepared by usual living anionic polymerization. Fig. 1 shows the ^1H NMR spectrum of the reaction product of the living polymer with *p*-CMS. In the spectrum of the reaction product of living poly(St) with *p*-CMS, the characteristic peaks based on the vinyl protons of the terminal styrene unit appear at 5.8 ppm.

The functionality of the terminal styrene unit of the macromonomer was estimated with the intensity ratio of methylene proton of the terminal vinyl group and methyl proton of *sec*-butyl group derived from the initiator. The functionality (*f*) could be estimated to be nearly unity ($f = 0.98$). The SSTM thus obtained was used for the graft copolymerization.

3.2. Graft copolymerization of St and SSTM

We used the SSTM with the M_n of 1100 and the M_w/M_n of 1.13 for the graft copolymerization with St. Copolymerization of St and SSTM with $CpTiCl_3$–MAO (MAO/Ti = 500 mole ratio) was conducted to synthesize the well-defined syndiotactic graft copolymers. The results are shown in Table 1. The copolymerization of St and the SSTM proceeded easily to give a copolymer. This is likely to be attributed to the open ligand structure with good accessibility of the catalyst in the copolymerization of the macromonomer.

The product was extracted with MEK to obtain a pure syndiotactic graft copolymer on the main chain from the resulting copolymer, since the syndiotactic graft copolymer are likely to be insoluble in MEK [1]. The results of MEK extraction of the copolymers are listed in Table 1. Considerable amount of the MEK-insoluble fraction was observed, and the MEK-insoluble fraction decreased with increasing the amount of SSTM in the feed.

In this copolymerization, the unpolymerized SSTM and atactic graft copolymer are possible to remain in the

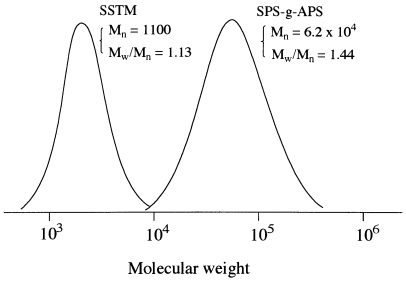

Fig. 2. GPC elution curves for the syndiotactic graft copolymer obtained with $CpTiCl_3$–MAO catalyst: SSTM and graft copolymer of MEK-insoluble fraction.

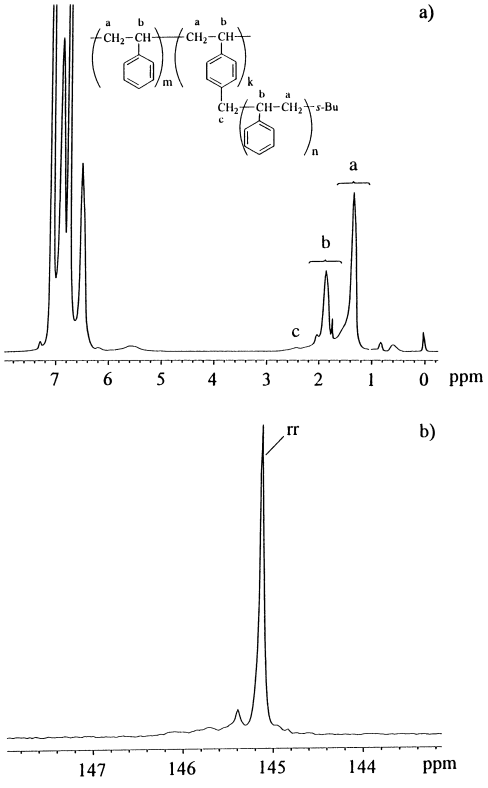

Fig. 3. ^1H and ^{13}C NMR spectra of the syndiotactic graft copolymer obtained with $CpTiCl_3$–MAO catalyst.

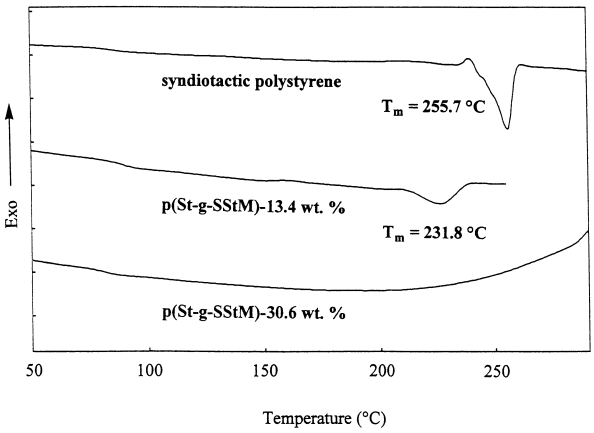

Fig. 4. DSC charts for the polymers during the second heating scan with a rate of 10°C/min.

MEK-insoluble fraction. To elucidate this point, GPC measurement was performed. The GPC elution curve for MEK-insoluble fraction obtained with the $CpTiCl_3$–MAO catalyst is shown in Fig. 2, in which the curve for SSTM is also depicted for comparison. From the elution curve, it was found that the unpolymerized SSTM did not remain in the MEK-insoluble fraction. The MEK-insoluble fraction revealed a unimodal curve, and the M_n and M_w/M_n of the polymer were 6.2×10^4 and 1.44, respectively. The MEK-soluble fraction contains a large amount of unpolymerized SSTM and only a small amount of the atactic graft copolymer. Thus, we regarded the MEK-insoluble fraction as polymer yield in this copolymerization.

The syndiotactic graft copolymer obtained with $CpTiCl_3$–MAO catalyst was characterized by the ^{13}C and ^1H NMR spectra as shown in Fig. 3. The peak of C_1 carbon in the phenyl group at 145.1 ppm based on syndiotactic sequence of St units were observed [1], and the signal based on C_1 carbon of the macromonomer that has atactic structure was also detected. From GPC measurement and the analysis of NMR spectra of the copolymer, we concluded that the SPS-*graft*-APS were synthesized.

The SSTM contents were calculated by the intensity ratio of the ^1H NMR spectrum based on the methylene protons of SPS and APS. The number of graft chains per polymer chain was also calculated using the SSTM contents and the M_n of the SSTM and of the resulting graft copolymer. It was estimated to be around 4 on the average, which is almost the same as the graft copolymer of the poly(St)-*graft*-poly(IP) as reported previously [8].

The DSC charts of the polymers are shown in Fig. 4. The melting point of the SPS-*graft*-APS containing SSTM of 13.4 mol% was observed at 231.8°C, which is lower than that of the SPS [2], indicating that a long branch chain introducing in the chain may disturb the crystallinity of the syndiotactic polystyrene on the main chain. When SSTM of 30.6 mol% was incorporated in the graft copolymer, no melting point was observed.

The SPS-*graft*-APS consists of the SPS on the main chain and APS on the side chain, and both the segments are miscible. This may be because there is no phase separation in the graft copolymer.

References

[1] Ishihara N, Seimiya T, Kuramoto M, Uoi M. Macromolecules 1986;19:2464.
[2] Po R, Cardi N. Prog Polym Sci 1996;21:47.
[3] Tsukahara Y. In: Salamone JC, editor. Polymeric materials encyclopedia, vol. 6. Boca Raton, FL: CRC Press, 1996:3918.
[4] Kaminsky W, Arndt M. Adv Polym Sci 1997;127:143.
[5] Chung TC, Lu HL, Ding RD. Macromolecules 1997;30:1272.
[6] Shiono T, Moriki Y, Soga K. Macromol Symp 1995;97:161.
[7] Henschke O, Neubauer A, Arnold M. Macromolecules 1997;26:8097.
[8] Endo K, Senoo K. Macromol Rapid Commun 1998;19:563.
[9] Asami R, Takaki M. Makromol Chem Suppl 1985;12:163.