

Syndiotactic Polymerization of Amino-functionalized Styrenes Using (Pentamethylcyclopentadienyl)titanatrane/MMAO Catalyst System[†]

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A set of unprecedented syndiospecific dimethyl- and diethylamino-functionalized polystyrenes was prepared by catalytically polymerizing the corresponding monomers using (pentamethylcyclopentadienyl)titanatrane/MMAO catalytic system. Dialkylamino-functionalized styrene monomers were synthesized by Wittig reaction from the corresponding aldehyde in high yield. The resulting polymers are soluble in polar organic solvents such as THF and show good thermal stability. The chemical transformation of the syndiospecific poly(4-diethylaminostyrene) also gave new polar polymers, namely syndiotactic poly(4-diethylaminostyrene hydrochloride), which is unattainable by traditional synthetic methods.

Key Words : Polystyrene, Poly(4-dimethylaminostyrene), Poly(4-diethylaminostyrene), Metallocene catalyst, Syndiospecific polymerization

Introduction

The development of the synthetic routes toward stereoregular functionalized polyolefins¹ which may have new properties in addition to the original properties of the polyolefins has been of scientific interest and a technologically important subject since the discovery of metallocene type catalysts.² But the known synthetic methods toward functionalized polyolefins are far from satisfaction.³ There are great difficulties in applying them directly for technology usage because Ziegler-Natta catalyst systems are intolerable to most functional groups due to their highly oxophilic nature.⁴

In 1992, Waymouth *et al.* showed that cationic metallocene catalysts could polymerize α -olefins containing silyl-protected alcohols and tertiary amines.⁵ Recently, they reported that polymerization of functionalized α -olefins gave rise to isotactic polymer with C_2 symmetric catalysts, to syndiotactic polymer with a C_s symmetric catalyst, and to atactic polymer with achiral catalyst precursors.⁶ In spite of these efforts, the preparation of stereoregular functionalized polystyrenes has not been well documented. There are only few reports about functionalized polystyrene copolymers with a small amount of functional comonomers such as 4-*t*-butyldimethylsilyloxystyrene, 4-aminostyrene, 4-hydroxystyrene and methacrylates.⁷ Prompted by this, we recently reported the syndiospecific homopolymerization of styrenes containing silyl-protected alcohol.⁸ In addition, Chung *et al.* also demonstrated the syndiospecific homopolymerization of amino-functionalized styrene with half-sandwich titanocene catalysts, Cp*TiMe₃ and Cp*TiCl₃, in the presence of various borate or MAO co-catalyst.⁹ However, their catalytic

systems showed some drawbacks such as the low polymer yield, the reduced catalytic activity, the relatively low syndiotacticity and the monomer discrimination. As to the monomer discrimination, only styrenes having amino groups indirectly attached to phenyl ring (having a spacer between phenyl ring and amino group) and a styrene containing sterically hindered amino group directly attached to phenyl ring are susceptible to the homopolymerization. In this regard, we employed (pentamethylcyclopentadienyl)titanatrane Cp*Ti(TEA) as a catalyst for the homopolymerization of 4-dialkylaminostyrenes (alkyl = methyl and ethyl) that lack a spacer between phenyl ring and amino group and have sterically less hindered amino group directly attached to phenyl ring. Half-sandwich titanocene catalytic systems Cp*TiCl₃/MMAO and Cp*Ti(OMe)₃/MMAO were also adopted as the control systems for comparison purpose. Reported herein are the accounts of the synthesis and characterization of new syndiotactic amino-functionalized polystyrenes.

Experimental Section

General Considerations. All reactions were carried out under an argon atmosphere using standard Schlenk and glove box techniques.¹⁰ Argon was deoxygenated with activated Cu catalyst (regenerated by heating to 300 °C under H₂ gas) and dried with drierite (Aldrich). All solvents were dried under a nitrogen atmosphere and distilled from sodium-potassium alloy/benzophenone ketyl (toluene, tetrahydrofuran (THF), diethylether) or CaH₂ (methylene chloride) and stored over the activated molecular sieves 3A.¹¹ Deuterated NMR solvents were used as received.

Measurements. ¹H and ¹³C{¹H}-NMR spectra of the polymers were recorded on a Bruker Spectrospin 400 spectrometer at room temperature. Elemental analyses were

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performed by Korea Basic Science Center, Seoul, Korea. Molecular weights of polymers were determined at room temperature in THF by means of a Waters 2690-HR1234 GPC calibrated with standard polystyrenes. The thermal stability of the polymers was measured by Thermal Analyst 200 TGA system under dinitrogen atmosphere at a rate of 10 °C/min. The melting temperature of the polymers was investigated by Thermal Analyst 200 DSC system under dinitrogen atmosphere at a heating rate of 20 °C/min. For each given polymerization run, at least two serial experiments were carried out to confirm the reproducibility of the formation of the polymer and the average values of these serial experimental results are given.

Syntheses. All chemicals were purchased from Aldrich. Modified methylaluminoxane (MMAO) (3A type) was supplied by Akzo Co. (Pentamethylcyclopentadienyl)-titanatrane ($\text{Cp}^*\text{Ti}(\text{TEA})$) was synthesized according to the literature procedure.¹²

4-Dimethylaminostyrene: BuLi (2.5 M solution in hexane, 11.2 mL, 28 mmol) was added dropwise to a stirred, cold (0 °C) solution of methyltriphenylphosphonium bromide (10.18 g, 28.5 mmol) in 50 mL of THF. After 10 min, a solution of 4-(dimethylamino)benzaldehyde (4.48 g, 30 mmol) in 50 mL of THF was added dropwise via needle. The yellow suspension was stirred for 4 h and treated with NH_4Cl . The solution was filtered and concentrated under vacuum. The resulting viscous liquid was purified by column chromatography using 10% ethylacetate in hexane as the solvent. The product was obtained as a colorless oil in a yield of 89% (3.93 g) and used immediately in the polymerization reaction. $^1\text{H NMR}$ (CDCl_3): δ = 7.40 (d, 2H, $-\text{C}_6\text{H}_4-$), 6.77 (d, 2H, $-\text{C}_6\text{H}_4-$), 6.72 (q, 1H, $-\text{CH} = \text{CH}_2$), 5.65 (dd, 1H, $-\text{CH} = \text{CH}_2$), 5.12 (dd, 1H, $-\text{CH} = \text{CH}_2$), 3.02 (s, 6H, $-\text{N}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, CDCl_3): δ = 150.2 ($-\text{CN}(\text{CH}_3)_2$), 136.6 ($-\text{CH} = \text{CH}_2$), 127.1 (Ph), 126.1 ($\text{C}-\text{CH} = \text{CH}_2$), 112.2 (Ph), 109.2 ($-\text{CH} = \text{CH}_2$), 40.39 ($-\text{N}(\text{CH}_3)_2$). EI-mass: m/z 148 (M^+).

4-Diethylaminostyrene: The title styrene was prepared in a yield of 91% (4.78 g) by reacting 4-diethylaminobenzaldehyde (5.32 g, 30 mmol) with methyltriphenylphosphonium bromide (10.18 g, 28.5 mmol) in a manner analogous to the procedure for 4-dimethylaminostyrene. $^1\text{H NMR}$ (CDCl_3): δ = 7.34 (m, 2H, $-\text{C}_6\text{H}_4-$), 6.70 (m, 3H, $-\text{C}_6\text{H}_4-$ and $-\text{CH} = \text{CH}_2$), 5.60 (dd, 1H, $-\text{CH} = \text{CH}_2$), 5.06 (dd, 1H, $-\text{CH} = \text{CH}_2$), 3.42 (q, 4H, $-\text{N}(\text{CH}_2\text{CH}_3)_2$), 1.22 (t, 6H, $-\text{N}(\text{CH}_2\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, CDCl_3): δ = 147.4 ($-\text{CN}(\text{CH}_2\text{CH}_3)_2$), 136.6 ($-\text{CH} = \text{CH}_2$), 127.3 (Ph), 125.1 ($\text{C}-\text{CH} = \text{CH}_2$), 111.5 (Ph), 108.6 ($-\text{CH} = \text{CH}_2$), 44.33 ($-\text{N}(\text{CH}_2\text{CH}_3)_2$), 12.56 ($-\text{N}(\text{CH}_2\text{CH}_3)_2$). EI-mass: m/z 175 (M^+).

Syndiotactic Poly(4-dialkylaminostyrenes): Polymerizations of 4-dialkylaminostyrenes (alkyl = methyl and ethyl) were carried out in 50 mL of toluene with the concentration condition of 0.42 M in styrene monomer, 0.20×10^{-3} M in $\text{Cp}^*\text{Ti}(\text{TEA})$ catalyst and an Al/Ti ratio of approximately 1000. Freshly prepared toluene stock solution of titanium catalyst was used. The amino-functionalized styrene, freshly

distilled toluene, MMAO and catalyst were loaded into a 250 mL Schlenk flask with magnetic stirring in that order at 50 °C. After 30 min of polymerization, the reaction was terminated by the addition of 50 mL of methanol. The resulting precipitated polymer was washed three times with 100 mL of methanol and dried in vacuo at 60 °C for 12 h.

Syndiotactic Poly(4-dimethylaminostyrene) (sPDMAAS): $^1\text{H NMR}$ (CDCl_3): δ = 6.58 (br, 4H), 2.89 (s, 6H), 1.92 (s, 1H), 1.41 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, CDCl_3): δ = 148.6, 134.9, 128.2, 112.8, 44.04, 41.01, 39.20. ($\text{C}_{10}\text{H}_{13}\text{N}$)_n (147.2194)_n. Calcd. C 81.59, H 8.90, N 9.51; Found C 82.11, H 9.10, N 9.48.

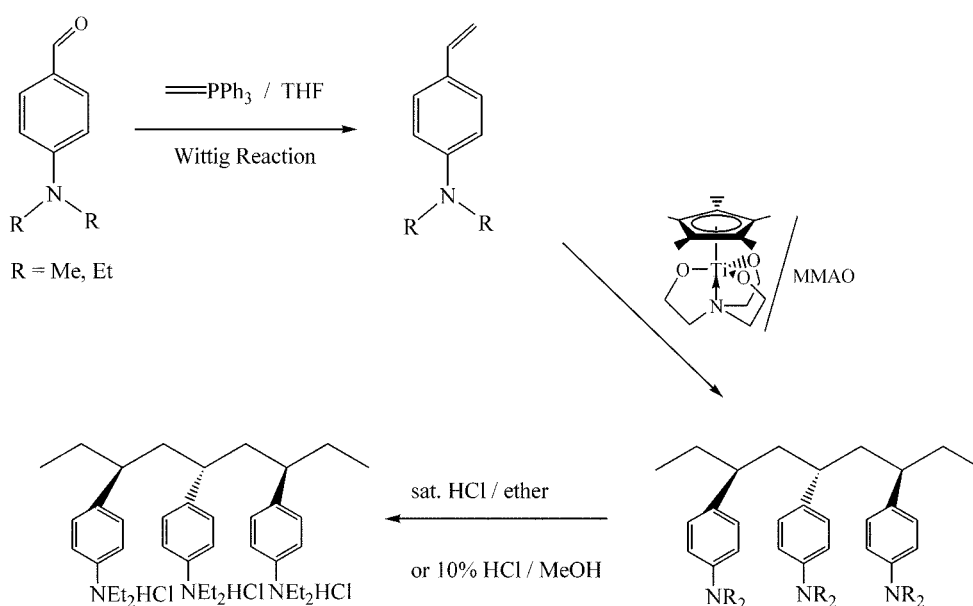
Syndiotactic Poly(4-diethylaminostyrene) (sPDEAS): $^1\text{H NMR}$ (CDCl_3): δ = 6.60 (br, 4H), 3.34 (s, 4H), 1.90 (s, 1H), 1.27 (s, 2H), 1.12 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, CDCl_3): δ = 148.7, 137.1, 131.7, 115.3, 47.48, 42.21, 16.05. ($\text{C}_{12}\text{H}_{17}\text{N}$)_n (175.273)_n. Calcd. C 82.23, H 9.78, N 7.99; Found C 82.44, H 10.09, N 7.88.

Syndiotactic Poly(4-diethylaminostyrene hydrochloride) (sPDEASHCl): 1.1 g of sPDEASHCl was prepared by treating sPDEAS (1.0 g) with 10% HCl/MeOH solution or saturated HCl/diethylether solution for 3 h. The resulting colorless precipitate was collected by filtration, washed with diethyl ether, and dried in vacuo. $^1\text{H NMR}$ (D_2O): δ = 7.29 (m, 2H), 6.62 (m, 2H), 3.62 (br, 4H), 1.60 (br, 3H), 1.03 (br, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, D_2O , ppm): δ = 147.9, 135.3, 130.8, 122.8, 55.09, 46.33, 41.37, 10.68.

Results and Discussion

Preparation of Functionalized Styrene Monomers. Two new functionalized-styrenes of 4-dimethylaminostyrene and 4-diethylaminostyrene as possible polymerization monomers were synthesized in order to make syndiotactic dialkylamino-functionalized polystyrenes. The preparation of the monomers was achieved by treating the corresponding functionalized benzaldehyde with Tebb reagent or by reacting the corresponding functionalized benzaldehyde with methyltriphenylphosphonium bromide and *n*-BuLi using Wittig reaction. The latter process is more efficient and quite general in terms of yield. As shown in Scheme 1, the double bond moiety of the functionalized styrene was introduced via the Wittig reaction to yield 4-dimethylaminostyrene or 4-diethylaminostyrene in quantitative yield based on the corresponding aldehyde. In order to remove excess triphenylphosphonium salts, the crude sticky oil was purified by column chromatography (SiO₂/10% ethylacetate in hexane) to give the desired product in 89-91% as a colorless oil.

Preparation and Characterization of Syndiotactic Amino-functionalized Polystyrenes. Besides $\text{Cp}^*\text{Ti}(\text{TEA})$,¹² we selected two more catalytic systems Cp^*TiCl_3 and $\text{Cp}^*\text{Ti}(\text{OMe})_3$ for comparison purpose out of the known active catalysts for syndiospecific polymerization of styrene such as CpTiX_3 (Cp = C_5H_5 , C_5Me_5 and X = halide, alkyl, alkoxy),¹³ (indenyl) TiCl_3 ¹⁴ and substituted indenyl derivatives,¹⁵ and carried out the homopolymerization of new amino-functionalized styrenes. Especially, the Lewis basic



Scheme 1

character of the trianionic triethoxyamine (TEA) ligand in $\text{Cp}^*\text{Ti}(\text{TEA})$ might render $\text{Cp}^*\text{Ti}(\text{TEA})$ catalyst less sensitive toward the Lewis basic substituents in functionalized styrenes and thus efficient catalyst. The polymerization results are summarized in Table 1.

For the preparation of syndiotactic polystyrene (sPS), all the three catalytic systems show extremely high activity (10^7 order of activity) although $\text{Cp}^*\text{Ti}(\text{TEA})$ and $\text{Cp}^*\text{Ti}(\text{OMe})_3$ whose polymerization behavior is similar are more efficient than Cp^*TiCl_3 in terms of yield, syndiotacticity and M_w . On the other hand, for the syndiospecific polymerization of amino-functionalized styrenes, $\text{Cp}^*\text{Ti}(\text{TEA})/\text{MMAO}$ is the best system among three catalysts in terms of the catalytic activity and the property of the resulting polymers. Surprisingly, $\text{Cp}^*\text{TiCl}_3/\text{MMAO}$ did not show any catalytic activity, implying that Cp^*TiCl_3 might be sensitive to polar functional groups such as amino groups in the polymerization. The syndiotactic polymers sPDMAS and sPDEAS from

$\text{Cp}^*\text{Ti}(\text{TEA})$ are soluble in polar solvents such as THF, CHCl_3 and methylene chloride. The molecular weights of sPDMAS and sPDEAS are $M_w = 38000$ with $M_w/M_n = 2.58$ and $M_w = 84000$ with $M_w/M_n = 4.55$, respectively. However, the poly(amino functionalized styrenes) from $\text{Cp}^*\text{Ti}(\text{OMe})_3$ are insoluble in any organic solvents and hence M_w for the polymers could not be determined. The syndiotacticity of the obtained polymers (measured by the insoluble portion in the refluxing 2-butanone) are much higher (94.2–99.5%) than the other reported results.⁹

The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of syndiotactic poly(4-dialkylaminostyrene) are shown in Figure 1 and Figure 2. In general, methine and *ipso*-phenyl carbons are sensitive to the microstructure of the polymer and used to interpret the stereospecificity of polymers.¹⁶ The methine, methylene and *ipso*-phenyl carbon signals appear at 39.20, 44.04 and 134.9 ppm, respectively for sPDMAS and at 42.21, 47.48 and 137.1 ppm, respectively for sPDEAS. The appearance of

Table 1. Polymerization data of functionalized styrene

Polymer	Catalyst	Yield (g)	Act./ 10^7	Yield. (%) ^d	SY ^e	M_w ^f	M_w/M_n ^f	DT ^g (°C)
sPS ^a	$\text{Cp}^*\text{Ti}(\text{TEA})$	3.4	2.4	74	99.1	105,000	2.4	364.6
	$\text{Cp}^*\text{Ti}(\text{OMe})_3$	4.0	2.8	87	98.0	133,000	1.7	364.0
	Cp^*TiCl_3	1.7	1.2	37	94.2	41,100	2.1	360.1
sPDMAS ^b	$\text{Cp}^*\text{Ti}(\text{TEA})$	1.7	1.7	55	98.2	38,000	2.6	199.4
	$\text{Cp}^*\text{Ti}(\text{OMe})_3$	0.74	0.7	24	99.4	n.d. ^h	n.d. ^h	199.2
	Cp^*TiCl_3	trace	—	—	—	—	—	—
sPDEAS ^b	$\text{Cp}^*\text{Ti}(\text{TEA})$	3.0	2.9	81	95.5	84,000	4.6	372.4
	$\text{Cp}^*\text{Ti}(\text{OMe})_3$	2.8	2.7	75	99.5	n.d. ^h	n.d. ^h	370.1
	Cp^*TiCl_3	trace	—	—	—	—	—	—

^aPolymerization Condition: Toluene = 100 mL, $T_p = 50^\circ\text{C}$, time = 10 min, Al/Ti = 1000, $[\text{Ti}] = 0.20 \times 10^{-3} \text{ M}$ (19.5 μmol), $[\text{Monomer}] = 0.44 \text{ M}$ (44 mmol). ^bPolymerization Condition: Toluene = 50 mL, $T_p = 50^\circ\text{C}$, time = 30 min, Al/Ti = 1000, $[\text{Ti}] = 0.20 \times 10^{-3} \text{ M}$ (9.8 μmol), $[\text{Monomer}] = 0.42 \text{ M}$ (21 mmol). ^cCatalytic Activity = g polymer/(mol catalyst mol monomer hr). ^dYield = (g polymer/g monomer) 100. ^eSyndiotacticity: insoluble portion in refluxing 2-butanone. ^fDetermined by gel permeation chromatography. ^gDecomposition temperature is defined by onset point of 5% degradation. ^hNot determined: insoluble in GPC solvents such as trichlorobenzene, *o*-dichlorobenzene or THF.

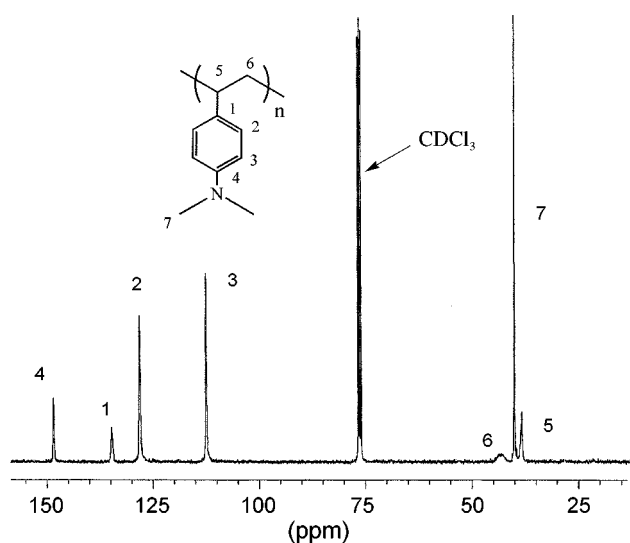


Figure 1. ^{13}C -NMR spectrum of syndiotactic poly(4-Dimethylaminostyrene).

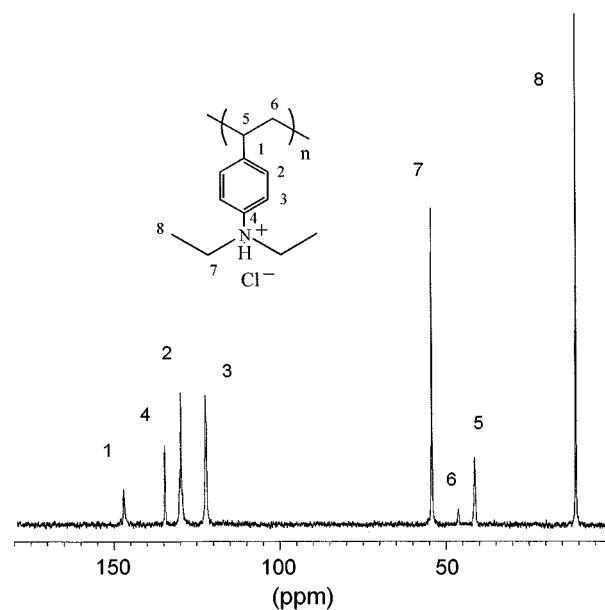


Figure 3. ^{13}C -NMR spectrum of syndiotactic poly(4-Diethylaminostyrene Hydrochloride).

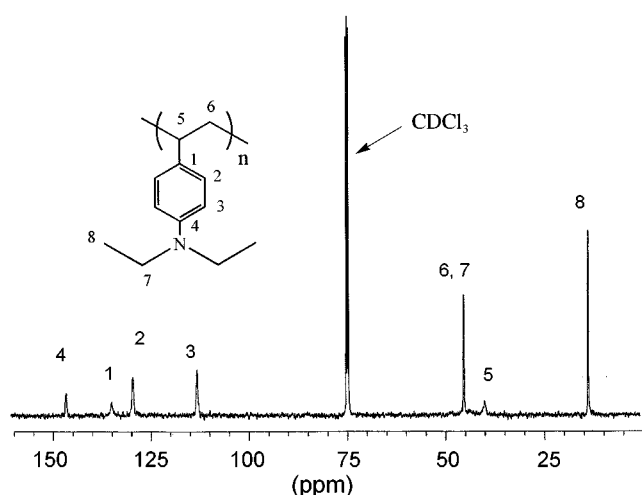


Figure 2. ^{13}C -NMR spectrum of syndiotactic poly(4-Diethylaminostyrene).

only one methine, methylene and *ipso*-phenyl carbon peak confirms the stereoregularity, though methylene carbon signal is overlapped with the methylene carbon signal of the ethyl group in the case of sPDEAS. In addition, the comparison of these data with the corresponding ^{13}C NMR signals of sPS at 125.6 (C4), 145.4 (C1 *ipso*-phenyl carbon), 128.1 (C2), 128.0 (C3), 43.68 (methylene carbon) and 40.51 (methine carbon) suggests the syndiotactic nature of the poly(amino functionalized styrenes). The observed large downfield chemical shift of carbon C4 from 125.6 ppm to 148.6 ppm (sPDMA) or to 148.7 ppm (sPDEAS), the large upfield shift of the *ipso*-phenyl carbons C1 from 145.4 ppm to 134.9 ppm (sPDMA) or to 137.1 ppm (sPDEAS) and C3 from 128.0 ppm (sPS) to 112.8 ppm (sPDMA) or to 115.3 ppm (sPDEAS) are consistent with the expected spectral change of the phenyl ring carbons caused by the introduction of a dialkylamino substituent at the phenyl carbon C4 of sPS. Due to the resonance effect, the introduction of a

dialkylamino group with electron donating inductive effect would cause a downfield chemical shift of the C4 carbon and an upfield chemical shift of carbons C1 and C3, leaving other carbons such as C2, methine and methylene carbons relatively unchanged.

In the case of sPDEAS whose methylene carbon signal is overlapped with the methylene carbon signal of the ethyl group, the confirmation of the stereoregularity was further attempted by reacting sPDEAS with 10% HCl/MeOH solution or saturated HCl/diethylether solution since the change of tertiary amine group into quaternary amine group would lead to the removal of an accidental overlapping. In fact, the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum (Fig. 3) of sPDEASHCl which is soluble in H_2O but insoluble in diethylether, THF or MeOH clearly shows the resolved feature of methylene carbon signals at 46.33 and 55.09 ppm. The appearance of the well resolved single signals for methine, methylene and *ipso*-phenyl carbons of sPDEASHCl in D_2O at 46.33, 41.37 and 147.9 ppm, respectively strongly indicates the syndiotactic nature of sPDEASHCl and thus of sPDEAS. The upfield appearance of C4 phenyl carbon signal compared to the *ipso*-phenyl carbon signal for sPDEASHCl in D_2O can be ascribed to the lack of resonance effect of triethylaminohydrochloride group. The foregoing NMR analyses clearly revealed that the $\text{Cp}^*\text{Ti}(\text{TEA})/\text{MMAO}$ system is a very efficient catalytic system for the preparation of syndiotactic amino-functionalized polystyrenes.

Thermal Properties of Functionalized Polystyrenes. The thermal stability is certainly a very important aspect in the functionalization of polymers since the preservation of thermal stability is desirable.¹⁷ Therefore, the obtained polymers have been investigated with respect to the thermal stability under dinitrogen atmosphere using TGA and their thermal stability properties were compared to that of pure

sPS. As indicated by the decomposition temperatures, 5% weight loss points, measured as 199.4 °C for sPDMA, 372.4 °C for sPDEAS and 364.6 °C for sPS. sPDEAS preserves thermal stability of sPS.

But as far as the melting point (T_m) concerns, the functionalization of syndiotactic polystyrene did not lead to the preservation. DSC measurements on the obtained polymers with sample weight of 2 mg did not show T_m . It is interesting to note that syndiotactic or isotactic poly(4-*n*-alkylstyrenes) did not show T_m regardless of the chain length of alkyl group.¹⁸ The possible strong intermolecular force induced by the substituents and thus the forbidden organization of main polymer chain were claimed as reasons for the absence of T_m .¹⁸ Furthermore, syndiotactic poly(4-*tert*-butyldimethylsilyloxystyrene) also did not show any T_m at DSC spectra.⁸ In addition, it is very interesting to note that the syndiotactic poly(4-(dimethylaminomethyl)styrene) shows a very weak T_m of 278 °C but syndiotactic poly(4-(*N,N*-bis(trimethylsilyl)aminomethyl)styrene) shows intense and high T_m of 330 °C at DSC spectra.⁹ It means methyl or ethyl substituents at amino group could prevent the formation of well-organized and uniform crystalline polymer structure.

Conclusion

In this paper, we have demonstrated the synthetic significance of the catalytic system of Cp*Ti(TEA)/MMAO in conducting syndiospecific homopolymerization of styrene containing tertiary amines as manifested by the preparation of syndiotactic polymers of 4-dimethylaminostyrene and 4-diethylaminostyrene. Their solubility in organic polar solvents and the high thermal stability indicate that the advantages of the functionalization of the styrene, the preservation of the desirable physical property of the original polymer as well as the development of the new chemical property, were achieved. In addition, the reaction of syndiotactic poly(4-diethylaminostyrene) with HCl afforded a new syndiotactic poly(4-diethylaminostyrene hydrochloride).

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