Polymer Bulletin 38, 43–48 (1997)

Polymer Bulletin

Polymerization of 4-*n*-alkylstyrenes with typical Ziegler-Natta and metallocene catalysts

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Received: 6 September 1996/Accepted: 16 October 1996

Summary

Polymerization of 4-*n*-alkylstyrenes (alkyl side group; methyl, ethyl, propyl and buthyl) was carried out with the η-$C_5(CH_3)_5TiCl_3$-methylaluminoxane (MAO) and $TiCl_3$-triethylaluminum (TEA) catalyst systems. When the η-$C_5(CH_3)_5TiCl_3$-MAO catalyst was used, the stereoregularity of resulting polymers markedly depended on the length of substituted alkyl groups, *i.e.*, the catalyst gave highly syndiotactic poly(4-methylstyrene), but produced atactic polymers for the monomers with ethyl, propyl and buthyl substituents. On the other hand, all the poly(4-n-alkylstyrene)s obtained with the $TiCl_3$-TEA catalyst were highly isotactic. As a result, a large difference was observed in the thermal properties of polymers obtained between the two catalyst systems.

Introduction

The syntheses and properties of poly(4-methylstyrene) and poly(styrene-*co*-methylstyrene) have been extensively investigated (1-4) to modify the thermo-mechanical properties of polystyrene. However, there are very few reports on the polymerization of 4-n-alkylstyrenes with longer substituted groups using the catalyst systems other than radical ones (5,6).

In the present study, we have synthesized various kinds of poly(4-n-alkylstyrene)s (alkyl side group; methyl, ethyl, propyl and buthyl) with different stereoregularity by using typical Ziegler-Natta and metallocene catalysts, *i.e.*, $TiCl_3$-triethylaluminum (TEA) and η-$C_5(CH_3)_5TiCl_3$-methylaluminoxane (MAO). This paper reports the results of polymerization together with some thermal properties of resulting polymers.

Experimental

Materials

Trichlorotitanium ($TiCl_3$), triethylaluminum (TEA) and methylaluminoxane (MAO) were commercially obtained and used without further purification. η-$C_5(CH_3)_5TiCl_3$ was synthesized according to the literature (7). Toluene, styrene and *4*-methylstyrene commercially obtained were further purified according to the usual procedures.

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4-Ethylphenylbromide. To a mixture of hydrobromic acid (16wt%, 200 mL) and 4-ethylaniline (61.6 mmol) at 273 K was added a solution sodium nitrite (63.5 mmol) in water (7.5 mL). After the mixture was kept at 273 K for 30 min, a solution of copper(I) chloride (69.7 mmol) in hydrobromic acid (16wt%, 69.7 mL) was added. The resulting mixture was heated at 343 K for one hour, cooled to room temperature and successively washed with aqueous KOH, hydrobromic acid (47wt%) and water. The organic layer was extracted with ether, dried over anhydrous $MgSO_4$ and evaporated to dryness. This crude product was purified by column chromatography on silica gel (MERCK Silica Gel 60, hexane in solvent), and characterized by ^{1}H-NMR (300 MHz, Varian Gemini 300 spectrometer) and IR (Jasco FT/IR-500). Yield 56%; ^{1}H-NMR ($CDCl_3$, ppm) δ 1.23 (t, 3H), 2.61 (q, 2H), 7.08 and 7.41 (AB system, 4H); IR (neat, cm^{-1}) 2965, 2931, 2871, 1486, 1072, 1010, 821.

4-*n*-Propylphenylbromide. 4-*n*-Propylphenylbromide was synthesized according to the same procedure as described above. Yield 48%; ^{1}H-NMR ($CDCl_3$, ppm) δ 0.92 (t, 3H), 1.61 (sext, 2H), 2.53 (t, 2H), 7.04 and 7.38 (AB system, 4H); IR (neat, cm^{-1}) 3030, 2960, 2940, 2870, 1480, 1010, 790.

4-*n*-Buthylphenylbromide. 4-*n*-Buthylbromide was also synthesized by the same method. Yield 54%; ^{1}H-NMR ($CDCl_3$, ppm) δ 0.91 (t, 3H), 1.34 (q, 2H), 1.56 (q, 2H), 2.53 (t, 2H), 7.06 and 7.39 (AB system, 4H); IR (neat, cm^{-1}) 3024, 2957, 2929, 2858, 1488, 1465,1073, 1011, 825, 516.

4-Ethylstyrene. To a mixture of Mg (8.12g, 334 mmol), ether (101 mL) and 4-ethylphenylbromide (228 mmol) was added a slice of iodine (ca. 5mg), followed by refluxing with stirring for 1h. The resulting mixture was then brought into contact with vinyl bromide in the presence of $NiCl_2$(dppp) (0.42 mmol, dppp = diphenylphosphinopropane) at 273 K for 30 min. The reaction was stopped with HCl (2N, 150 mL), followed by extracting with ether. The organic layer was successively washed with water, aqueous $NaHCO_3$ and again with water. The final organic layer was dried over anhydrous $MgSO_4$, evaporated and distilled under 20 mmHg at 358-360 K. Yield 42 %; ^{1}H-NMR ($CDCl_3$, ppm) δ 1.20 (t, 3H), 2.65 (q, 2H), 5.18, 5.70 and 6.71 (ABC system, 3H), 7.18 and 7.33 (q, AB system, 4H); IR (neat, cm^{-1}) 3085, 3005, 2965, 2930, 1629, 1511, 1454, 1406, 989, 903, 836.

4-*n*-Propylstyrene. 4-*n*-Propylstyrene was synthesized according to the same procedure. Yield 53%; b. p. 374-376 K /18 mmHg; ^{1}H-NMR ($CDCl_3$, ppm) δ 0.96 (t, 3H), 1.61 (q, 2H), 2.59 (t, 2H), 5.20 and 5.72 (q, 2H), 6.71 (q, 4H), 7.15 and 7.35 (q, AB system, 4H); IR (neat, cm^{-1}) 3085, 3020, 2959, 2930, 2871, 1629, 1511, 1454, 1405, 989, 903, 843, 820.

4-*n*-Buthylstyrene. 4-*n*-Buthylstyrene was also synthesized by the same method. Yield 48%; b. p. 389-391 K /15 mmHg; ^{1}H-NMR ($CDCl_3$, ppm) δ 0.95 (t, 3H), 1.36 (m, 2H), 1.61 (q, 2H), 2.61 (t, 2H), 5.20 and 5.72 (q, 2H), 6.71 (q, 4H), 7.15 and 7.35 (q, AB system, 4H); IR (neat, cm^{-1}) 3085, 3020, 2957, 2929, 1629, 1510, 1456, 1405, 988, 902, 839.

Polymer Synthesis and Characterization

Polymerization was carried out in a 100 mL glass reactor equipped with a magnetic stirrer under nitrogen atmosphere and terminated by acidic methanol.

The ^{13}C-NMR spectra operated at 75.5 MHz were recorded with a Varian Gemini 300 spectrometer at 373 K on 10 % (w/v) solutions in 1,2,4-trichlorobenzene/C_6D_6. The molecular weight and molecular mass distribution (MMD) of polymers were determined by gel permeation chromatography Senshu Scientific SSC-7100 at 403K using *o*-dichlorobenzene as the solvent. Differential scanning calorimetry (DSC) measurements were made using a Mettler DSC820 instrument under nitrogen atmosphere. All samples (10-15 mg) encapsulated in the aluminum pans were heated at 563 K for 5 min and quenched into a liquid nitrogen bath in DSC equipment. The thermograms of quenched samples were measured at a heating rate of 20 K/min.

Results and Discussion

The results of polymerizations with both the η-$C_5(CH_3)_5TiCl_3$-MAO and $TiCl_3$-TEA catalyst systems are summarized in Tab. 1. The metallocene catalyst showed much higher activity for every monomer. Among the monomers used in the present study, 4-methylstyrene gave the highest yield with both catalysts, which may be attributed to the electron donating effect of methyl group. In general, the polydispersity ($\overline{M}_w / \overline{M}_n$) of polymers obtained with the η-$C_5(CH_3)_5TiCl_3$-MAO catalyst is relatively narrow reflecting the single site character. However, poly(4-methylstyrene) displays a broad MMD, the reason of which is not clear at the moment.

Tab. 1. Yields and molecular weights of poly(4-*n*-alkylstyrene)s obtained with η-$C_5(CH_3)_5TiCl_3$-MAO and $TiCl_3$-TEA

cat.	monomer	rate $\times 10^{-2}$ in polymer $\times$ g/(Ti $\times$ g)	$M_w \times 10^{-4}$ [a]	M_w/M_n [a]
η-$C_5(CH_3)_5TiCl_3$	St[b]	19.7	12.8	2.3
	MeSt[b]	37.2	16.0	5.1
	EtSt[c]	22.3	2.2	2.4
	PrSt[c]	7.1	7.5	2.0
	BuSt[d]	9.4	6.0	2.6
$TiCl_3$	St[e]	2.3	91.0	4.6
	MeSt[e]	3.5	304.8	10.0
	EtSt[f]	0.9	14.6	2.0
	PrSt[f]	0.6	93.1	7.6
	BuSt[g]	0.3	n.d.[h]	n.d.[h]

[a] Calculated from GPC curves. [b] Polym. conditions: monomer=174 mmol, Mt=3×10^{-2} mmol, MAO=13.5 mmol, polym. temp. 313 K, time 24h, no solvent. [c] 1/4 scale of b). [d] 1/7 scale of b). [e] Polym. conditions: monomer=174 mmol, Mt=5.0×10^{-1}mmol, TEA=3.5 mmol, polym. temp. 343 K, time 2h, toluene 20 mL. [f] 1/8 scale of e). [g] 1/4 scale of e). [h] no detect.

Fig. 1 shows the ^{13}C-NMR spectra of polystyrene and poly(4-alkylstyrene)s obtained with the η-$C_5(CH_3)_5TiCl_3$-MAO catalyst. The [rr] triad fraction was estimated from the phenyl C1 peak (Tab. 2). The syndiotacticity of polystyrene and poly(4-alkylstyrene) are extremely high as reported already (8), whereas those of the other polymers are very low.

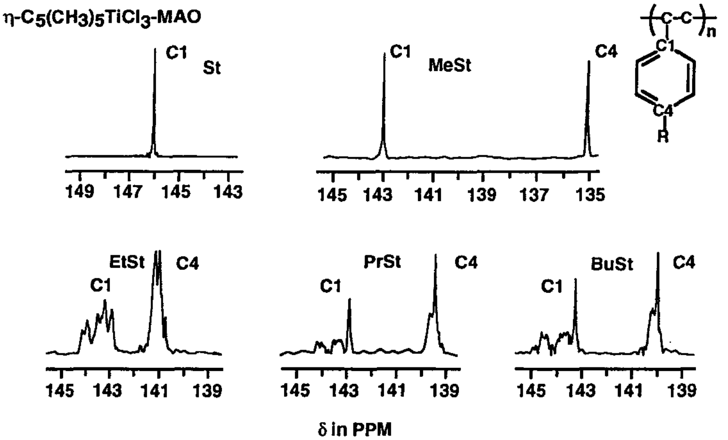

Fig. 1 ^{13}C-NMR spectra of poly(4-n-alkylstyrene)s obtained with η-$C_5(CH_3)_5TiCl_3$-MAO catalyst. St: polystyrene, MeSt: poly(4-methylstyrene), EtSt: poly(4-ethylstyrene), PrSt: poly(4-propylstyrene), BuSt: poly(4-butylstyrene).

Zambelli *et. al.* (9,10) demonstrated that syndiotactic polymerization of styrene proceeds by 2,1-insertion as shown in Fig.2. In the cases of 4-*n*-alkylstyrenes with longer alkyl substituted groups, the bulky substituted groups might impose a retarding effect on such a η^4-coordination.

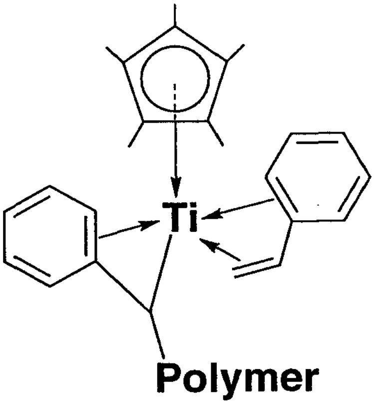

Fig. 2 A plausible model of syndiotactic styrene polymerization proposed by Zambelli[10)].

Contrary to those observations, the conventional heterogeneous Ziegler-Natta catalyst gave isotactic polymers independently of the size of substituted groups (Fig. 3). The results seem to be not surprising, considering that the polymerization takes place over chiral active species. Whereas, the apparent activity drastically decreased with an increase in the bulkiness of substituted groups, probably due to steric effect of the incoming monomer to the growing chain ends.

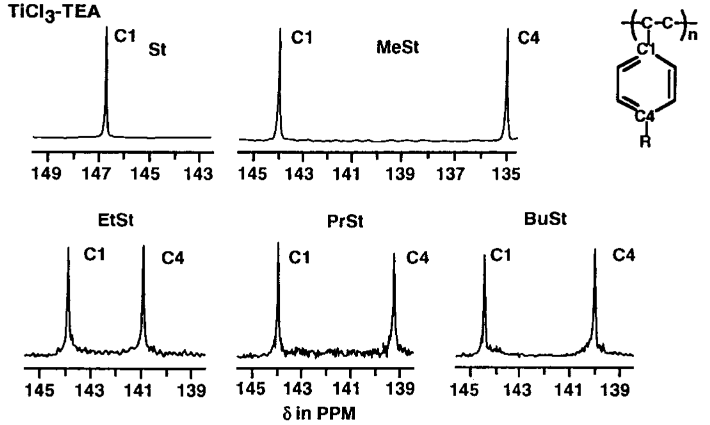

Fig.3 ^{13}C-NMR spectra of poly(4-n-alkylstyrene)s obtained with $TiCl_3$-TEA catalyst. St: polystyrene, MeSt: poly(4-methylstyrene), EtSt: poly(4-ethylstyrene), PrSt: poly(4-propylstyrene), BuSt: poly(4-butylstyrene).

The melting points (T_m) and glass transition temperatures (T_g) of polymers produced with both catalysts are shown in Tab. 2. The T_g of polymers except poly(4-methylstyrene) showed a tendency to decrease with increasing the carbon number of substituted groups, which is responsible for the magnitude of excess free volume per chain caused by the substituents.

Tab. 2. Stereoregularity and thermal properties of poly(4-*n*-alkylstyrene)s

cat.	monomer	triad fraction in %			T_g	T_m
		[rr]	[rm]	[mm]	/ K	/ K
η-$C_5(CH_3)_5TiCl_3$	St	> 99	—	—	372 (372)[a)]	544 (495)[a)]
	MeSt	> 99	—	—	383 (387)	— (—)
	EtSt	32	44	24	356 (350)	— (402)
	PrSt	44	36	20	324 (327)	— (404)
	BuSt	43	33	24	298 (303)	— (403)

[a)] For the isotactic polymers obtained with the $TiCl_3$-$AlEt_3$ catalyst.

The exceptionally high T_g of poly(4-methylstyrene) can be understood in terms of inter-molecular force originating from a strong electron donating effect of methyl group. It is of interest that the T_g is not affected so much by the stereoregularity of polymers. As to the melting point (T_m), on the other hand, both the syndiotactic and isotactic poly(4-methylstyrene)s showed no melting point. The absence of T_m may be also related to the electron donating effect of methyl group, *i.e.*, the organization of main chains is forbidden by a strong inter-molecular force. Indeed, a large difference was observed between the chemical shifts of phenyl C1 and phenyl C4 for poly(4-methylstyrene) (Figs. 1 and 3), proving an existence of strong electron donating effect of methyl group.

In conclusion, several kinds of poly(4-n-alkylstyrene)s with different stereoregularity were synthesized using the typical Ziegler-Natta and metallocene catalysts, and the thermal properties of resulting polymers were analyzed in some detail.

Acknowledgement

This work was supported by the Grant-in-Aid for Scientific Research on Priority Area No. 08751024 from Ministry of Education, Science and Culture, Japan.

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