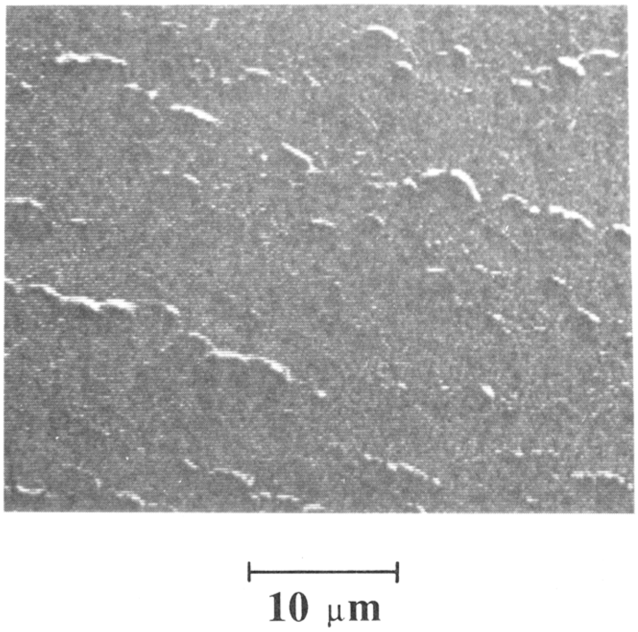

Figure 5. SEM of the glass slide after PCTFE–OC(O)NH-$(CH_2)_3Si(OEt)_3$ has been peeled off.

indicate the compositional structure.

PCTFE–OC(O)NH$(CH_2)_3$Si$(OEt)_3$—Glass Adhesion. Attempts to form adhesive joints between polymer films and glass were carried out between Mylar film in a laboratory hydraulic press with applied heat and pressure. PCTFE, PCTFE–OH, and PCTFE–OC(O)NH$(CH_2)_3$Si-(O)OH show no tendency to adhere to glass under various experimental conditions varying from 80 to 120 °C for up to 24 h. Polymer films fell when the glass slide was inverted. PCTFE–OC(O)NH$(CH_2)_3$Si$(OEt)_3$ samples, on the other hand, adhere tenaciously to glass when bonding was carried out at 80 °C for 12 h. The film could not be peeled from the glass without tearing it, indicating cohesive failure in the polymer film. XPS and SEM of glass surfaces after the films were peeled also indicate cohesive failure in the polymer (Figures 4 and 5).

We ascribe the adhesive bond strength between the polymer film sample and glass to covalent bonds. The evidence that covalent bonding exists between the polymer film and the coupling agent through a urethane linkage is strong, indicated by spectroscopic characterization of PCTFE–OC(O)NH$(CH_2)_3$Si$(OEt)_3$. We have no direct evidence confirming that condensation between polymer surface Si$(OEt)_3$ groups and glass Si–OH groups occurs (eq 1). The control experiments with PCTFE–OH and PCTFE–OC(O)NH(CH_2)3Si(O)OH (which have no surface Si$(OEt)_3$ groups), however, indicate that this condensation is the likely source of the strong adhesion.

Polymer–Polymer Adhesion. Adhesion tests similar to those discussed above were performed between all combinations of PCTFE–OH, PCTFE–OC(O)NH-$(CH_2)_3$Si$(OEt)_3$, and PCTFE–OC(O)NH$(CH_2)_3$Si(O)OH. No strong adhesion occurred between any of the film samples, but impressive differences were observed. Two PCTFE–OH samples do not adhere to one another, they fall apart. The other combinations form adhesive joints that are weak relative to PCTFE–OC(O)NH$(CH_2)_3$Si-$(OEt)_3$–glass, and the films can be separated by modest pressure, indicating apparent adhesive failures.

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(10) PCTFE–OH does not react with $H_2N(CH_2)_3Si(OEt)_3$ in THF at room temperature for 4, h as evidenced by XPS, ATR IR, and contact analyses.

Stereospecific Polymerization of Styrene Giving the Syndiotactic Polymer

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ABSTRACT: A mixture of titanium compounds ($TiCl_4$, $Ti(OEt)_4$, or $(\eta\text{-}C_5H_5)TiCl_3$) with methylaluminoxane catalyzes the polymerization of styrene, even above room temperature, to the pure syndiotactic polystyrene, which has a narrow molecular weight distribution ($M_w/M_n = 2$). Pure syndiotactic polymers are also obtained with ring-substituted styrenes. Monomer reactivity is enhanced by electron-releasing substituents on the aromatic ring.

Introduction

The control of stereoregularity is of practical importance in the development of new polymers or tailor-made polymers and in the control of polymer properties. Since the discovery of the Ziegler–Natta catalyst systems in the early 1950s, extensive studies concerning the stereospecific polymerization of olefins have been carried out.[1,2] In most cases, isotactic polymers are obtained, and syndiotactic polymers are rare.

In principle, polystyrene can occur with isotactic, atactic, or syndiotactic configurations, but the latter was unknown until very recently.[3,4]

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In a previous paper,[5] we reported the first example of a syndiotactic polystyrene (SPS), with a very high syndiotacticity, with over 94% racemic heptad configuration, and with a high degree of crystallinity; it crystallized in a planar zigzag conformation with the periodicity of 5.06 Å.

By use of our catalyst mixture containing a titanium compound and a methylaluminoxane, SPS can be obtained even above room temperature. We propose that the mechanism of this polymerization is quite different from both that of syndiotactic polymerization at low temperature, which proceeds by a radical pathway, and that of polymerization by certain Ziegler–Natta catalysts, which produce syndiotactic polypropylene at temperatures below -65 °C.[6-9]

Furthermore, when various ring-substituted styrenes are polymerized by our catalyst system, the corresponding syndiotactic polystyrenes are produced. In the present paper, we describe the polymerization of styrene to a syndiotactic polymer and the effects of ring substituents.

Experimental Section

Materials. Most metal compounds and alkylaluminum compounds were commercially available and were used without further purification. Certain titanium compounds were synthesized according to the literature.[10]

Polymerization grade styrene was supplied by Idemitsu Petrochemical Co., Ltd. Reagent grade toluene was dried and purified by being passed through columns of 4A and 13X molecular sieves; it was finally stored under argon atmosphere.

Methylaluminoxane was prepared as follows: In a 500-mL flask equipped with a mechanical stirrer and an argon inlet were placed 35.5 g of $CuSO_4 \cdot 5H_2O$ and 200 mL of toluene. Neat trimethylaluminum was added very slowly in a dropwise manner at 20 °C. After stirring for 24 h the mixture was filtered, and the filtrate was concentrated under reduced pressure. The resulting solid residue was dissolved in 2 mol/L toluene.

Polymerization Procedure. A four-necked glass flask equipped with a mechanical stirrer was used for polymerization. Various proportions of toluene, the alkylaluminum compounds (alkylaluminum and water or methylaluminoxane), the metal compound, and styrene were charged to the flask, in this order, under an argon atmosphere. The addition of styrene was taken as the start of the polymerization reaction. The polymerization reactions were stopped at intervals by addition of acidified methanol. The resulting polymer was washed with 500 mL of methanol several times and dried at 80 °C in vacuo for 2 h.

Analyses. Gel permeation chromatograms of the polymers were obtained at 135 °C by using a Waters Model 150C GPC. The solvent was 1,2,4-trichlorobenzene, and the flow rate was 1.0 cm^3/min.

The ^{13}C NMR spectra of syndiotactic polymers were recorded at 130 °C in 1,2,4-trichlorobenzene by using a JNMGX-270 spectrometer.

Results and Discussion

The results of the polymerization of styrene using different metal compounds with methylaluminoxane as cocatalyst are given in Table I. With methylaluminoxane as the cocatalyst, the titanium halide compounds (e.g., $TiCl_4$ and $TiBr_4$), titanium compounds lacking halogen atoms (e.g., $Ti(OC_2H_5)_4$ and $Ti(OC_4H_9)_4$), and titanium compounds with sterically demanding ligands (e.g., titanium acetylacetonate and $(\eta\text{-}C_5(CH_3)_5)_2TiCl_2$) all produce SPS. Not only Ti(IV) but also Ti(III) compounds, such as $(\eta\text{-}C_5H_5)TiCl_2$, give SPS.

When mono(cyclopentadienyl)titanium derivatives were used as catalysts, the yield of SPS was high and was independent of the steric bulk; i.e., both $(\eta\text{-}C_5H_5)TiCl_3$ and $(\eta\text{-}C_5(CH_3)_5)TiCl_3$ gave the same amount of SPS. However, bis(cyclopentadienyl)titanium derivatives gave only low yields of SPS, which were also independent of steric bulk. This suggests that two cyclopentadienyl groups hinder the reaction. Polymer conversion was found to vary according to the ligand environment around titanium.

Table I
Polymerization of Styrene Using Various Metal Compounds with Methylaluminoxane[a]

metal compds	Al unit, mol	conversion, wt %	structure
$TiCl_4$	0.04	4.1	syndiotactic
$TiBr_4$	0.04	2.1	syndiotactic
$Ti(OCH_3)_4$	0.04	3.8	syndiotactic
$Ti(OC_2H_5)_4$	0.04	9.5	syndiotactic
$(\eta\text{-}C_5H_5)TiCl_2$	0.03	44.1	syndiotactic
$(\eta\text{-}C_5H_5)TiCl_3$	0.015	68.2	syndiotactic
	0.03	99.2	syndiotactic
$(\eta\text{-}C_5(CH_3)_5)TiCl_3$	0.005	6.5	syndiotactic
	0.015	36.7	syndiotactic
	0.03	75.4	syndiotactic
	0.045	100	syndiotactic
$(\eta\text{-}C_5H_5)_2TiCl_2$	0.03	1.0	syndiotactic
$(\eta\text{-}C_5(CH_3)_5)_2TiCl_2$	0.03	2.0	syndiotactic
$(\eta\text{-}C_5(CH_3)_5)_2TiClH$	0.03	8.8	syndiotactic
$Ti(acac)_2Cl_2$[b]	0.04	0.4	syndiotactic
$ZrCl_4$	0.04	0.4[c]	atactic
$(\eta\text{-}C_5H_5)_2ZrCl_2$	0.04	1.3[c]	atactic
$(\eta\text{-}C_5H_5)_2HfCl_2$	0.04	0.7[c]	atactic
$(\eta\text{-}C_5H_5)_2VCl_2$	0.04	0.7[c]	atactic
$V(acac)_3$	0.01	0.4[d]	atactic
$Nb(OC_2H_5)_5$	0.04	0.2[c]	atactic
$Ta(OC_2H_5)_5$	0.04	trace[c]	atactic
$Cr(acac)_3$	0.01	1.4[d]	atactic
$Co(acac)_3$	0.01	1.8[d]	atactic
$Ni(acac)_2$	0.01	80.8[d]	atactic

[a] Polymerization conditions: metal compounds, 5×10^{-5} mol; styrene, 0.2 mol; toluene, 100 mL; 50 °C, 2 h. [b] acac = acetylacetonato. [c] Styrene, 1.57 mol; toluene, 100 mL. [d] Metal compounds, 2.5×10^{-5} mol; styrene) 0.43 mol; toluene, 100 mL.

Table II
Polymerization of Styrene Using $(\eta\text{-}C_5H_5)TiCl_3$ with Various Organoaluminum Compounds[a]

organic Al compds, mol	yield, g	conversion, wt %	structure
	0.8	0.5	atactic
TMA[b] (5×10^{-3})	0.1	0.5	atactic
TMA (0.04) + H_2O (0.04)	17.6	10.8	syndiotactic
TEA[c] (0.04) + H_2O (0.04)	0.8	0.5	syndiotactic
Malox[d] (0.04)	14.9	9.2	syndiotactic
Malox (0.02) + TMA (0.02)	7.1	4.4	syndiotactic
Malox (0.02) + TEA (0.02)	0.3	0.2	syndiotactic
Malox (0.02) + TIBA[e] (0.02)	15.5	9.5	syndiotactic
Malox (0.02) + DEAC[f] (0.02)	5.0	3.1	atactic
Clalox[g] (0.04)	94.8[h]	100	atactic

[a] Polymerization condition: $(\eta\text{-}C_5H_5)TiCl_3$, 5×10^{-5} mol; styrene, 1.57 mol; 50 °C, 2 h; toluene, 100 mL. [b] Trimethylaluminum. [c] Triethylaluminum. [d] Methylaluminoxane. [e] Triisobutylaluminum. [f] Diethylaluminum chloride. [g] Chloroaluminoxane. [h] Polymerization condition: styrene, 0.87 mol.

Pure SPS was not formed by any of the other metal compounds studied, for example, vanadium compounds, which produce syndiotactic polypropylene. Furthermore, the well-known Kaminsky catalyst[11] ($(\eta\text{-}C_5H_5)_2ZrCl_2$/methylaluminoxane) did not give SPS. Only titanium compounds give the pure syndiotactic product. It has sometimes been suggested titanium is isotactic specific and vanadium is syndiotactic specific, yet in the present catalyst system it is titanium which is syndiotactic specific.

The results of polymerizations of styrene using $(\eta\text{-}C_5H_5)TiCl_3$ with various organoaluminum compounds are given in Table II.

By use of the catalyst system of $(\eta\text{-}C_5H_5)TiCl_3$ without methylaluminoxane, or the catalyst system of $(\eta\text{-}C_5H_5)$-

Table III
Polymer Yield and Molecular Weights of Polymers Produced after Different Polymerization Times with the (η-C_5H_5)$TiCl_3$/Methylaluminoxane System[a]

polymerization time, h	rate × 10^3, g of SPS/(g of Ti·h)	$10^{-4}/\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$
0.33	16.20	3.18	1.99
0.67	13.41	2.80	2.21
1.0	11.42	2.80	1.93
1.5	6.41	2.72	2.13
2.0	6.38	2.99	2.01
3.0	6.07	2.62	2.23

[a] Polymerization conditions: 50 °C, styrene, 0.15 mol; (η-C_5H_5)$TiCl_3$, 1.25×10^{-5} mol; Al unit 7.5×10^{-3} mol; toluene, 100 mL. [b] Calculated from GPC curves.

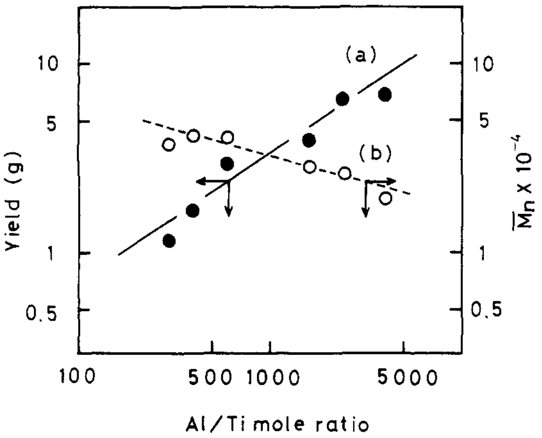

Figure 1. Influences of Al/Ti molar ratio on polymer yield and number-average molecular weight. The (η-C_5H_5)$TiCl_3$/methylaluminoxane system is used: (η-C_5H_5)$TiCl_3$, 1.25×10^{-5} mol; Al unit, 7.5×10^{-3} mol; styrene, 0.15 mol; toluene, 100 mL; 50 °C, 1 h.

$TiCl_3$ with trimethylaluminum instead of methylaluminoxane, SPS could not be obtained. In contrast, with the catalyst system of (η-C_5H_5)$TiCl_3$ with trimethylaluminum and water, with methylaluminoxane (which was synthesized as described above), or with methylaluminoxane mixed with a trialkylaluminum SPS was obtained.

When (η-C_5H_5)$TiCl_3$ with methylaluminoxane mixed with an alkylaluminum system was used, SPS could be obtained. The activity was enhanced by the type of alkylaluminum used with the methylaluminoxane.

However, when a haloalkylaluminum such as $Al(C_2H_5)_2Cl$ or an aluminoxane having a chloro group instead of a methyl group was used, only an atactic polystyrene was produced by cationic polymerization.[12,13]

The time dependence of the polymerization rate when the (η-C_5H_5)$TiCl_3$/methylaluminoxane catalyst system is used is shown in Table III. The polymerization rate decreases with an increase in polymerization time. This behavior of the polymerization rate is similar to that of Ziegler–Natta catalyst systems, and the decrease may be attributed to the deactivation of the active centers or to the occlusion of part of the catalyst in the precipitating polymer.

The time dependence of the number-average molecular weight ($\bar{M}_n$) and the molecular weight distribution of polymers produced is also shown in Table III. The number-average molecular weight remained almost constant during the course of the polymerization. This indicates that chain-transfer reactions exist in the present polymerization system. Also, the polydisperisity ($\bar{M}_w/\bar{M}_n$) of polymers remained almost constant, at approximately 2.0, which was close to the theoretical value of a homogeneous Ziegler–Natta catalyst system, indicating that the catalyst system under discussion is homogeneous.[14]

Table IV
Polymer Yield, Overall Activation Energy, and Molecular Weights of Polymer Produced at Different Polymerization Temperatures with the (η-C_5H_5)$TiCl_3$/Methylaluminoxane System[a]

polymerization temp, °C	yield, g	$10^{-4}\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$	E,[c] kcal/mol
5	1.04	14.90	1.74	
20	3.28	9.71	1.92	
50	7.64	2.99	2.01	7.6
65	5.92	0.96	2.57	
85	4.16	0.65	2.05	

[a] Polymerization conditions: polymerization period, 2 h; styrene, 0.15 mol; (η-C_5H_5)$TiCl_5$, 1.25×10^{-5} mol; Al unit, 7.5×10^{-3} mol; toluene, 100 mL. [b] Calculated from GPC curves. [c] Overall activation energy.

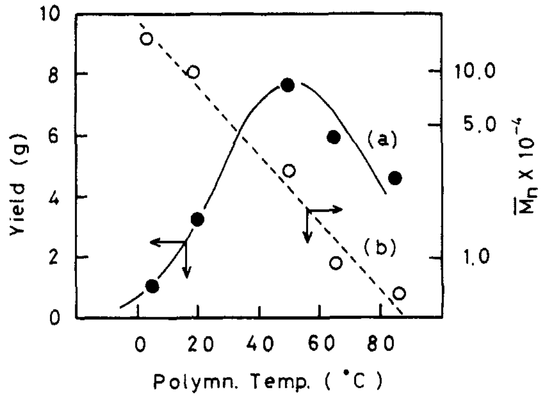

Figure 2. Influences of polymerization temperature on polymer yield and on number-average molecular weight. The (η-C_5H_5)$TiCl_3$/methylaluminoxane system is used: (η-C_5H_5)$TiCl_3$, 1.25 × 10^{-5} mol; Al unit, 7.5×10^{-3} mol; styrene, 0.15 mol; toluene, 100 mL; 2 h.

Figure 1a shows the relation between the concentration of methylaluminoxane (the mole ratio of methylaluminoxane to (η-C_5H_5)$TiCl_3$) and the yield of polymers produced. The yield of polymer increased with an increase in the Al/Ti molar ratio and with a very high Al/Ti ratio. This dependence of the yield of polymers produced on the Al/Ti ratio, especially at high Al/Ti, was similar to the behavior observed during polymerization of olefins using methylaluminoxane.[11]

The influence of the Al/Ti molar ratio on the number-average molecular weight of polymers produced is shown in Figure 1b. The number-average molecular weight was dependent on the mole ratio of methylaluminoxane to (η-C_5H_5)$TiCl_3$, presuming that a chain-transfer reaction with methylaluminoxane takes place.

Figure 2a and Table IV show the relation between polymerization temperature and the yield of polymers produced. Under 50 °C, the yield of polymers increased with an increase in polymerization temperature. This temperature dependence on yield may be attributed to the large equilibrium constant for the monomer adsorption. Over 50 °C, the yield of polymer decreased with an increase in polymerization temperature. This decrease is attributed to decomposition of the catalyst or to deactivation of the active centers.

In a radical pathway, syndiotactic polymer is normally produced only at very low temperatures. However, the present catalyst systems give the syndiotactic polymer even at high temperature, and the tacticity was almost unchanged. The apparent activation energy of syndiotactic polymerization of styrene using this catalyst system (7.6

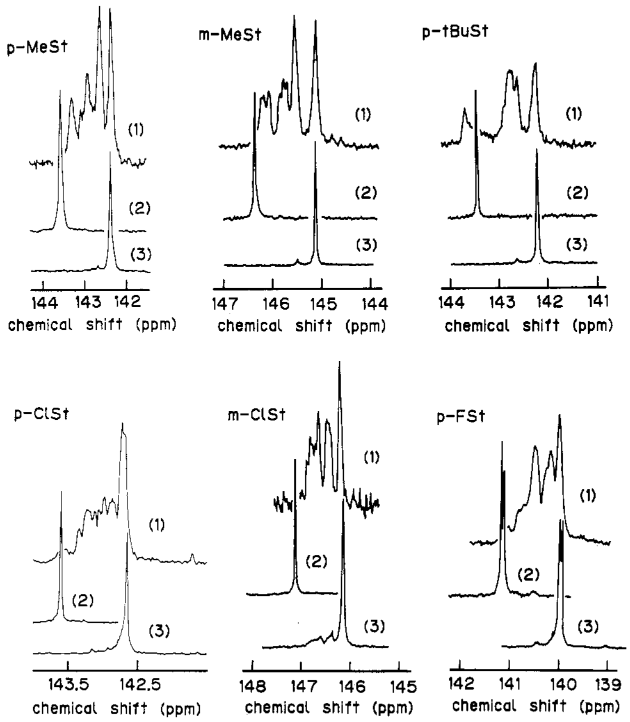

Figure 3. ^{13}C NMR spectra of poly(ring-substituted styrene): (1) atactic (AIBN); (2) isotactic (Mg-supported $TiCl_4/Al(C_2H_5)_3$); (3) syndiotactic ((η-$C_5H_5)TiCl_3$/methylaluminoxane).

kcal/mol) was as low as that of isotactic polymerization of styrene using the $TiCl_3/Al(C_2H_5)_3$ system.[15] From these results, it is proposed that the mechanism of this catalyst system is not the normal radical pathway but that the mechanism proceeds according to a coordination polymerization process.

Figure 2b and Table IV show the relation between polymerization temperature and the number-average molecular weight of the polymers produced. The number-average molecular weight of the polymers decreased with an increase in polymerization temperature, indicating that the chain-transfer reaction is enhanced by an increase in temperature.

When the various ring-substituted sytrenes were polymerized by using the (η-$C_5H_5)TiCl_3$/methylaluminoxane system, the corresponding syndiotactic polystyrenes were obtained. The new poly(ring-substituted)styrenes thus obtained were examined by ^{13}C NMR, as well as the corresponding atactic polystyrenes prepared with 2,2′-azobisisobutyronitrile and the corresponding isotactic polystyrene produced with Mg-supported $TiCl_4/Al(C_2H_5)_3$.

Figure 3 shows ^{13}C NMR spectra of the phenyl C-1 carbon of the three different configurations of each poly(ring-substituted) sytrene: e.g., the alkylstyrenes, poly(*p*-methylstyrene), poly(*m*-methylstyrene), poly(*p*-*tert*-butylstyrene); the halogenated styrenes, poly(*p*-chlorostyrene), poly(*m*-chlorostyrene), *and* poly(*p*-fluorostyrene).

The spectrum of each atactic poly(ring-substituted) styrene (Figure 3 (1)) shows many main peaks corresponding to their various configurational sequences. These spectra are the same as that of atactic PS.[5] The spectrum of each isotactic poly(ring-substituted)styrene (Figure 3 (2)) shows a single sharp peak at a lower magnetic field corresponding to the *mmmm* pentad configuration. These spectra are the same as that of isotactic PS.[5] In contrast, the chemical shifts of the phenyl C-1 carbon in each new poly(ring-substituted)styrene are observed at higher magnetic field (Figure 3 (3)), and the peak of each, except poly(*p*-fluorostyrene), is single and sharp. These spectra are the same as that of syndiotactic PS.[5] In poly(*p*-fluorostyrene), the peak at higher magnetic field is split, due to coupling to the ^{19}F nuclear.

From these results, we conclude that the corresponding syndiotactic polystyrene also could be obtained by using the (η-$C_5H_5)TiCl_3$/methylaluminoxane system.

The melting points (T_m) of syndiotactic poly(ring-substituted)styrene and the corresponding isotactic polymer are given in Table V. Almost all of the syndiotactic polymers produced have a high degree of crystallinity. As shown in Table V all the T_m values of syndiotactic polymers are higher than those of isotactic polymers with the corresponding substituent.

Table V

T_g and T_m of Syndiotactic and Isotactic Polystyrene Derivatives Obtained

	syndiotactic[a]		isotactic[b]	
monomer	T_g, °C	T_m, °C	T_g, °C	T_m, °C
St[c]	100	266	99	224
m-MeSt	72	206	71	125
p-MeSt	106	173	101	
p-^{t}BuSt	137	310	125	308
m-FSt	86	275		
p-FSt	94	322	101	247
m-ClSt	85	192	84	124
p-ClSt	124	299	124	165
p-BrSt	131			

[a] Polymerization conditions: (η-$C_5H_5)TiCl_3$, 5×10^{-5} mol; Al unit, 0.03 mol; monomer, 0.75 mol; 20 °C, 120 h; toluene, 100 mL. [b] Polymerization conditions: Mg-supported $TiCl_4$, 1×10^{-4} mol; $Al(C_2H_5)_3$, 2×10^{-3} mol; monomer, 0.75 mol; 20 °C, 120 h; heptane, 10 mL. [c] St, styrene; *p*-MeSt, *p*-methylstyrene; *m*-MeSt, *m*-methylstyrene; *p*-^{t}BuSt, *p*-*tert*-butylstyrene; *p*-FSt, *p*-fluorostyrene; *m*-FSt, *m*-fluorostyrene; *p*-ClSt, *p*-chlorostyrene; *m*-ClSt, *m*-chlorostyrene; *p*-BrSt, *p*-bromostyrene.

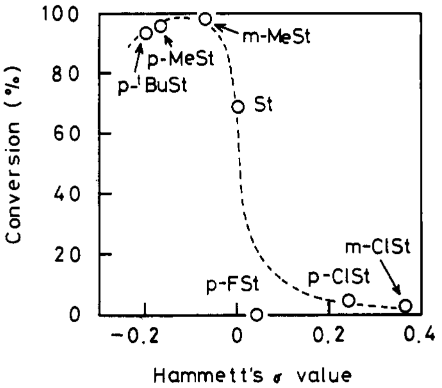

Figure 4. Relation between the Hammett σ value for each substituent and reactivities in polymerization: (η-$C_5H_5)TiCl_3$, 5×10^{-5} mol; Al unit, 0.03 mol; monomer, 0.2 mol; toluene, 100 mL; 50 °C, 3 h.

Figure 4 shows the relation between the Hammett σ value of each substituent and reactivities in polymerization. It is observed that monomer reactivity is enhanced by electron-releasing substituents in an aromatic ring. Even when *p*-*tert*-butylstyrene with a substituent of large steric hindrance was polymerized, the monomer reactivity was high. This indicates that there is a strong polar effect of the substituent on the rate of addition. A more precise study of the mechanism of insertion of styrene is in progress.

Registry No. TMA, 75-24-1; TEA, 97-93-8; TIBA, 100-99-2; syndiotactic St, 28325-75-9; isotactic St, 25086-18-4; syndiotactic *m*-MeSt, 54193-23-6; isotactic *m*-MeSt, 30847-60-0; syndiotactic *p*-MeSt, 54193-24-7; isotactic *p*-MeSt, 54190-46-4; syndiotactic *p*-*t*-BuSt, 107911-20-6; isotactic *p*-*t*-BuSt, 30998-04-0; syndiotactic *m*-FSt, 54193-26-9; syndiotactic *p*-FSt, 54193-27-0; isotactic *p*-FSt,

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53745-75-8; syndiotactic *m*-ClSt, 107830-48-8; isotactic *m*-ClSt, 116002-24-5; syndiotactic *p*-ClSt, 62319-29-3; isotactic *p*-ClSt, 29297-96-9; syndiotactic-*p*-BrSt, 107911-22-8; $TiCl_4$, 7550-45-0; $TiBr_4$, 7789-68-6; $Ti(OCH_3)_4$, 992-92-7; $Ti(OC_2H_5)_4$, 3087-36-3; $(\eta\text{-}C_5H_5)TiCl_2$, 31781-62-1; $(\eta\text{-}C_5H_5)TiCl_3$, 1270-98-0; $(\eta\text{-}C_5(CH_3)_5)TiCl_3$, 12129-06-5; $(\eta\text{-}C_5H_5)_2TiCl_2$, 1271-19-8; $(\eta\text{-}C_5(CH_3)_5)_2TiCl_2$, 11136-36-0; $(\eta\text{-}C_5(CH_3)_5)_2TiClH$, 115912-71-5; $Ti(acac)_2Cl_2$, 17099-86-4; H_2O, 7732-18-5.

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Near Monodisperse Ethylene–Propylene Copolymers by Direct Ziegler–Natta Polymerization. Preparation, Characterization, Properties

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ABSTRACT: In Ziegler copolymerization of ethylene and propylene, appropriate premixing of aluminum alkyl and vanadium catalyst components prior to contacting with the monomers can give essentially instantaneous initiation. Transfer and termination reactions at temperatures below 40 °C are slow enough, compared to propagation, to permit very narrow molecular weight distribution (MWD) polymer (M_z:M_w:M_n $\sim$ 1.3:1.2:1.0) to be formed in a plug flow reactor. Due to the different reactivity of the monomers, the polymer has a tapered compositional distribution. This can be shown by fractionation of the polymer prior to and after thermal degradation, with compositional analysis of the fractions. Chain lifetimes in the polymerization are of the order of seconds. The narrow MWD produces obvious changes in rheological properties as compared to EPM produced in a conventional backmixed reactor, yielding behavior typical of high plateau modulus, anionically prepared, hydrogenated polyisoprenes. In the linear viscoelastic region steady-state compliances can be measured with the product of the compliance and plateau modulus $J_e{}^0G_N{}^0 = 3.5$. The dependence of the normalized loss modulus G''/G''_{max} versus frequency is "typical" of monodisperse hydrogenated polyisoprenes and polybutadienes. This is the first report of the preparation of such "statistical" ethylene–propylene copolymers at practical polymerization temperatures, i.e. higher than −40 °C, and with both ethylene and propylene present in the initiation step.

Introduction

Ziegler–Natta polymerizations are carried out commercially on a grand scale. Billions of pounds of polyolefin plastics and elastomers are produced annually. Regardless of the polymerization process, these polymers are characterized by molecular weight distributions (MWD) as broad as or broader than the most probable, i.e. M_z:M_w:M_n $\sim$ 3:2:1. This is a result of a number of factors including reactor residence time distribution, number of catalyst species present, and the interrelationship of initiation, propagation, termination, and transfer reactions. In the case of ethylene–propylene copolymerization all commercial producers employ backmixed reactors[1-3] which, in the case of a single catalyst species, will produce a most probable MWD, with uniform composition along the individual chain contours. For product performance improvements in selected applications it is advantageous to prepare narrow MWD versions of these polymers with varied intramolecular compositional distributions.

On the laboratory scale, Doi[4-8] and co-workers have produced narrow MWD polypropylene and poly(propylene–ethylene) propylene block copolymers at temperatures below −50 °C with a "living" Ziegler system based on vanadium acetylacetonate. Following Doi, Evens and Pijpers[9] polymerized propylene at −78 °C and also attempted to make block polymers. In the presence of ethylene both sets of workers find that the very narrow MWD's (<1.2 M_w/M_n) obtained with pure propylene tend to be broadened somewhat. These results were obtained in batch polymerizations. At low temperature, propylene sequences tend to become syndiotactic.

Junghanns et al.,[10] as part of a larger study, examined ethylene–propylene copolymerization in a tubular reactor with $VOCl_3/Et_3Al_2Cl_3$ catalyst. These studies were carried out at ambient temperature and above. Product characterization indicated that the MWD was narrower than that produced in a backmixed reactor, but no quantitative data were given. Also with use of $VOCl_3$, and in addition VCl_4, Doi and co-workers[11] were unsuccessful in attempts to prepare narrow MWD polypropylene. Their failure presumably was due to initiation or convective mixing problems.

In this paper we report on a procedure for preparing ethylene–propylene copolymers at temperatures up to 50 °C with a narrower MWD than obtained previously. To make narrow MWD polymer, initiation must be rapid compared to chain propagation and both these reactions in turn should be fast compared to termination or transfer. Furthermore the residence time distribution in the reacting medium must be that of a batch or plug flow reactor. We

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