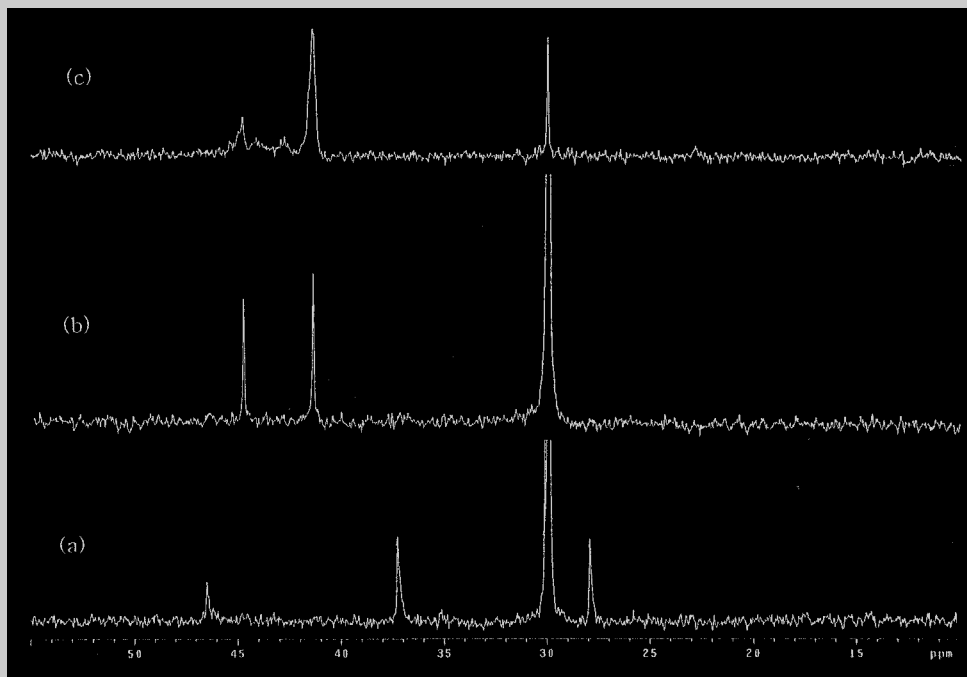**Full Paper:** Copolymerization of ethylene and styrene was carried out with CpTiCl₃/MgCl₂-PMAO as a catalyst at various temperatures and comonomer concentrations. The present catalyst system produces a pseudorandom copolymer of ethylene and styrene beside syndiotactic poly(styrene) (sPS) and poly(ethylene) (PE). The copoly-

mers were obtained at temperature $\geq 60\,^\circ$C, indicating the active species promoting the copolymerization being formed at elevated temperatures. On the other hand, styrene incorporation in the copolymer increases progressively with the increase of styrene concentration.

^{13}C NMR spectra of benzene-soluble (a) and benzene-insoluble (b) fraction of copolymerization product prepared with CpTiCl₃/MgCl₂ catalyst

Copolymerization of ethylene and styrene with a MgCl₂-supported CpTiCl₃ catalyst

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Introduction

Most of the conventional Ziegler-Natta catalysts fail to incorporate more than 1 mol-% of styrene (S), when used for ethylene (E) styrene copolymerization. The resulting polymers show a substantially polyethylenic structure containing a low amount of styrene[1,2]. The recent developments in homogeneous Ziegler-Natta catalysis, how-

ever, enabled the synthesis of E–S copolymers[3–5] of various compositions and structures.

Copolymerizations of ethylene and styrene using simple catalytic systems like CpTiCl₃-MAO have been previously reported[3,6]. The copolymerization reactions depend on the reaction conditions, in particular, on the Al/Ti molar ratio: at a high Al/Ti ratio, a mixture of

poly(ethylene) and syndiotactic poly(styrene), or at most block copolymers, were produced, whereas at low Al/Ti ratios, E–S copolymers containing up to 35% of styrene were obtained[3]. On the contrary, other recent reports denied the production of E–S copolymer in the presence of CpTiCl₃-MAO[7]. The polymer obtained was not a true copolymer but a mixture of poly(styrene) and poly(ethylene).

A Dow patent[8] disclosed the synthesis of "pseudorandom" E–S copolymers using bridged monocyclopentadienylamido titanium complexes as catalysts. On the other hand, Kakugo et al.[9, 10] reported that a catalyst based on 2,2′-thiobis(4-methyl-6-tert-butylphenoxy)titanium dichloride and MAO affords a fractionable mixture of syndiotactic polystyrene (sPS) and an alternating E–S copolymer. Nevertheless, Inoue et al.[11] reported that pseudorandom E–S copolymers can be obtained using ansa-zirconocene based catalysts. Further alternating E–S copolymers have also been synthesized by Pellecchia et al.[12] and Arai et al.[13] using a MAO-free half-metallocene catalyst and ansa-metallocene catalysts, respectively. More recently, the synthesis and characterization of E–S copolymers obtained from titanium-based complexes were reported by Xu et al.[14, 15] and Mülhaupt et al.[16], respectively.

In a previous paper[17], we reported that monocyclopentadienyl titanium (CpTiCl₃) that was supported on activated MgCl₂ using a novel precipitation method showed high activity for polymerization of ethylene in the presence of polymethylaluminoxane (PMAO). In this article, an attempt was made to copolymerize ethylene with styrene using the MgCl₂-supported catalyst[17]. The properties of these polymers were examined.

Experimental part

Materials

Ethylene (from Korea Petrochemical Ind. Co., 99.5% purity) was used without further purification. Nitrogen of an extra pure grade (from Korea Petrochemical Ind. Co., 99.999% purity) was dried by passing it through a column containing molecular sieve 3A. Toluene (Matsuneon Chemicals., Ltd.) was refluxed 48 h over sodium and distilled under nitrogen atmosphere. Styrene was dried over CaH₂ for one hour and distilled under reduced nitrogen pressure. Polymethylaluminoxane (PMAO, 9.5 wt.-% in toluene) (from Tosoh Akzo Corp.) was used without further purification. The MgCl₂-supported CpTiCl₃ catalyst (Ti, 3.4 wt.-%) was synthesized according to the previous paper[17].

Copolymerizations

The copolymerization runs were carried out at atmospheric pressure of ethylene in a 200-mL glass reactor equipped with a magnetic stirrer. The reactor was charged under nitrogen sequentially with toluene, styrene, and PMAO; the inert gas was removed and the polymerization mixture was saturated with ethylene, which was continuously fed during the run, and thermostated in an oil bath at the onset temperature. The copolymerization reaction was started by adding the catalyst. The copolymerization was terminated by the addition of a dilute solution of hydrochloric acid in methanol. The precipitated polymer was filtered, washed with an excess of methanol, and dried under vacuum.

Analysis

To remove the homopolymers selective solvent fractionation was performed using a Soxhlet extractor. In detail boiling methyl ethyl ketone (MEK) and boiling benzene[6, 14, 18] were applied sequentially.

The melting (T_m) and the crystallization temperatures (T_c) of the obtained polymers were measured by means of differential scanning calorimetry (DSC, PERKIN-ELMER Pyris1). The DSC traces were recorded between 30 °C and 300 °C at a heating rate of 10 °C/min. ¹³C NMR spectra were recorded on a Varian Unity-Inova-300 spectrometer operating at 299.71 MHz in the Fourier transform mode at 130 °C. A 1,2,4-trichlorobenzene/benzene-d₆ mixture was used as solvent (8/2). $\bar{M}_w$ (weight-average molecular weight) and $\bar{M}_w/\bar{M}_n$ (molecular weight distribution) of the polymers were determined by means of GPC (gel permeation chromatography, Waters 150-CV) in 1,2,4-trichlorobenzene at 135 °C, and the data were analyzed using poly(styrene) calibration curves.

Results and discussion

Copolymerizations of ethylene (E) with styrene (S) were carried out under various conditions using CpTiCl₃/ MgCl₂-MAO as catalyst system[17]. The main results are summarized in Tab. 1 and 2, whereas details of the polymerizations are reported in the Experimental part.

To determine homopolymer and/or copolymer in the copolymerization products, selective solvent fractionation was carried out successively using boiling MEK for the removal of atactic poly(styrene) (aPS) and boiling benzene for the removal of E–S copolymer from syndiotactic poly(styrene) (sPS) and poly(ethylene) (PE) homopolymers. It was found that MEK was a good solvent for atactic PS, whereas benzene was a poor solvent for syndiotactic PS and PE homopolymer but, however, a good solvent for E–S copolymers. The amounts of MEK-soluble fractions were negligible (≤0.3%), and the amounts of MEK-insoluble fractions were higher than 99.7%, indicating that the production of atactic polystyrene was negligible. The copolymerization products were analyzed by means of ¹³C NMR and DSC as shown in Fig. 1 and Tab. 1 and 2.

Runs 1 to 5 were performed at elevated temperatures in toluene with ethylene at atmospheric pressure and styrene at constant amount as shown in Tab. 1. The copolymerization product obtained at 20 °C is insoluble in benzene
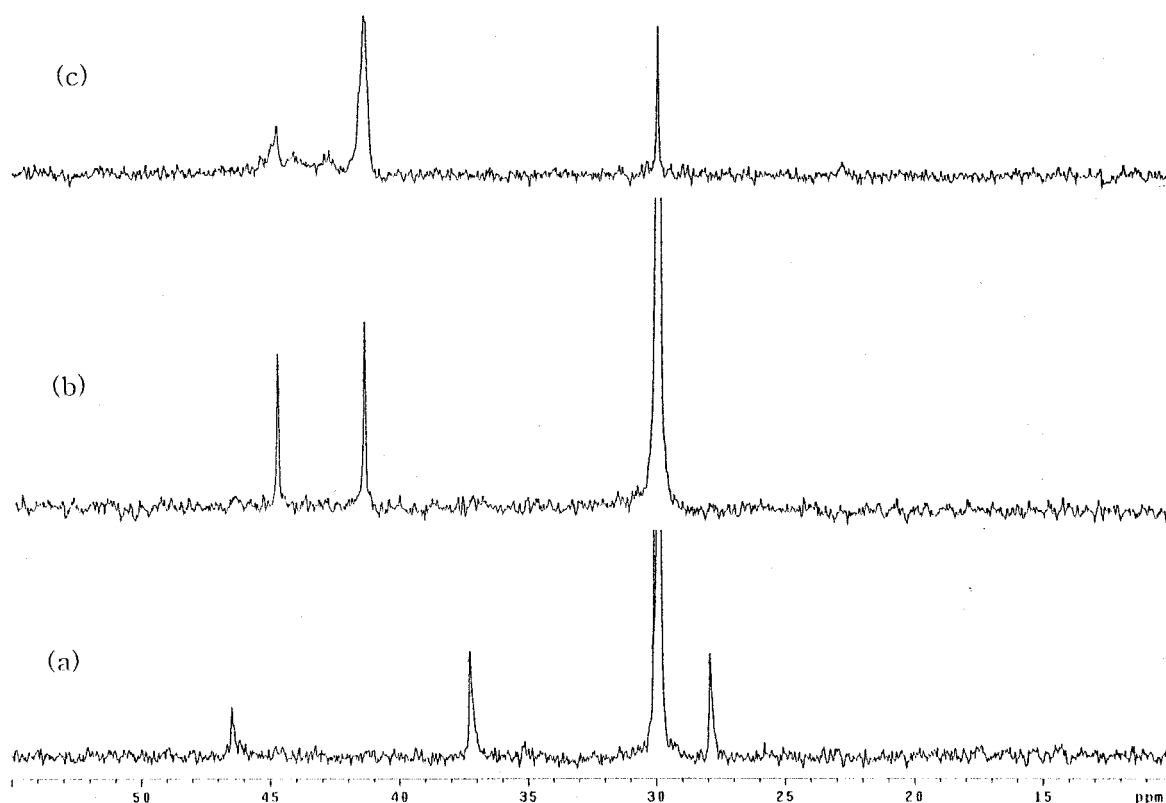
Fig. 1. ^{13}C NMR spectra of benzene-soluble (a) and benzene-insoluble (b) fraction of copolymerization product prepared with CpTiCl$_3$/MgCl$_2$ catalyst, and a crude copolymerization product (c) prepared with CpTiCl$_3$ catalyst

and consists essentially of poly(ethylene) (NMR spectrum of benzene-insoluble fraction displays a strong single resonance at 29.9 ppm and T_m is 131.2 °C), whereas those obtained at 40, 60, 80, and 100 °C show a more complex composition. The benzene-soluble fraction shows a much lower melting temperature (T_m) than those of typical sPS and PE homopolymers. In contrast, the benzene-insoluble fraction displays two distinct melting temperatures and crystallization temperatures (T_c) which coincide with the respective T_m's and T_c's of PE and sPS homopolymers. These results indicate that the benzene-soluble fraction of the copolymerization product is a E−S copolymer, while the benzene-insoluble fraction is a blend of sPS and PE homopolymers. The aliphatic regions of the ^{13}C NMR spectra of benzene-insoluble and benzene-soluble fraction are given in Fig. 1 as an example. In the NMR spectrum (b) of the benzene-insoluble fraction, only three peaks could be found at 44.8, 41.4 and 29.9 ppm. Two peaks at 44.8 and 41.4 ppm are assigned to the secondary carbon (S$_{\alpha\alpha}$) and tertiary carbon (T$_{\beta\beta}$) in the syndiotactic styrene sequence. The peak at 29.9 ppm is assigned to S$_{\alpha\alpha}$ in the ethylene sequence. These results indicate that the benzene-insoluble fraction is a mixture of syndiotactic poly(styrene) and poly(ethylene) homopolymers. The NMR spectrum of the benzene-soluble fraction was quite different in comparison with

the benzene-insoluble fraction. In the NMR spectrum (a) of the benzene-soluble fraction, four resonance peaks were observed at 46.5, 37.2, 29.9, and 27.9 ppm can be assigned to T$_{\delta\delta}$, S$_{\alpha\delta}$, S$_{\delta\delta}$, and S$_{\beta\delta}$ in the E−S copolymer sequence[5, 6, 12, 14]. From these results, it is concluded that copolymerization of ethylene and styrene with the present catalyst system gives a mixture of E−S copolymer, poly(ethylene), and syndiotactic poly(styrene).

As apparent from Tab. 1, it was found that the composition of the copolymerization products depended strongly on the polymerization temperature. Only poly(ethylene) (PE) was obtained at 20 °C. A small amount of the E−S copolymer was obtained at 40 °C, although syndiotactic poly(styrene) (sPS) was also produced. The weight fraction of the E−S copolymer as well as the copolymerization activity showed a maximum value at 60 °C. The catalytic activity then decreased at 80 °C. The amount of sPS homopolymer increased with increasing temperature, whereas the amount of PE homopolymer decreased. The variation of the composition of copolymerization products with temperature indicates that the formation and type of active sites depend on the polymerization temperature. The results are in agreement with those of Xu et al[14].

The infuence of styrene incorporation on the melting (T_m) and the crystallization temperature (T_c) were investi-

Tab. 1. Copolymerization[a] of ethylene (E) and styrene (S) using CpTiCl₃/MgCl₂-MAO catalyst at different temperatures

Run	Temp. $\frac{}{°C}$	Activity[b] $\times 10^{-6}$	C₆H₆-soluble (MEK-insoluble) fraction				C₆H₆-insoluble fraction			
			Yield $\frac{}{\%}$	T_m $\frac{}{°C}$	T_c $\frac{}{°C}$	Styrene[d] incorp. $\frac{}{\text{mol-\%}}$	Yield $\frac{}{\%}$	T_m $\frac{}{°C}$	T_c $\frac{}{°C}$	Styrene[d] content $\frac{}{\text{mol-\%}}$
1	20	0.52	0	–	–	–	100	131.2	115.0	0
2	40	0.55	trace	–	–	–	100	128.0, 261.7	115.3, 224.3	1.2
3	60	1.07	4.8	88.7	74.6	6.2	95.2	126.2, 259.4	111.6, 223.4	3.4
4	80	0.65	4.0	92.9	78.8	4.6	96.0	126.6, 260.3	112.3, 224.2	6.1
5	100	0.05	2.9	107.5 (248.4)[g]	83.7 (206.9)[g]	3.4	97.1	129.1, 259.4	115.0, 231.8	23.5

[a] Polymerization conditions: catalyst = 14.2 µmol of Ti, Al/Ti(mol/mol) = 420, toluene = 100 mL, time = 1 h, styrene = 1.46 mol/L, ethylene pressure = 1 atm.
[b] g of polymer/mol of Ti · atm · h.
[c] Weight percent of benzene-soluble fraction.
[d] Estimated from ¹³C NMR spectra of E−S copolymer.
[e] Weight percent of benzene-insoluble fraction.
[f] Estimated from ¹³C NMR spectra of the benzene-insoluble fraction.
[g] Weak peak of sPS homopolymer.

Tab. 2. Copolymerization[a] of ethylene (E) and styrene (S) using CpTiCl₃/MgCl₂-MAO as catalyst at different monomer concentration

Run	[Styrene] in the feed $\frac{}{\text{mol/L}}$	Activity[b] $\times 10^{-6}$	Comp. of copolymer products (wt.-%)			E−S copolymer		
			E−S[c]	PE[d]	sPS[d]	Styrene $\frac{}{\text{mol-\%}^{e}}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
6	0.79	1.25	4.2	92.7	3.1	3.9	2.5	3.9
7	1.46	1.07	4.8	91.8	3.4	4.8	3.2	3.8
8	2.01	1.01	5.3	91.4	3.3	5.4	4.9	4.3
9	2.49	0.96	5.2	89.9	4.9	6.8	6.2	4.5
10	2.91	0.81	3.9	89.6	6.5	9.0	7.3	4.1
11[f]	2.01	0.02	–	19.9	80.1	–	–	–

[a] Polymerization conditions: see Tab. 1, polymerization temperature = 60 °C.
[b] g of polymer/mol of Ti · atm · h.
[c] Calculated from the benzene-soluble fraction.
[d] Estimated from ¹³C NMR spectra of the benzene-insoluble fraction.
[e] Estimated from ¹³C NMR spectra of the benzene-soluble fraction.
[f] CpTiCl₃ as catalyst was used under the same polymerization conditions.

gated. Only 3.4 mol-% of styrene incorporation was sufficient to lower the T_m from 131.2 °C, typical for poly-(ethylene), to 107.5 °C. Even lower melting temperatures were detected with 92.9 °C and 88.7 °C for 4.6 mol-% and 6.2 mol-% styrene incorporation, respectively. A similar trend with respect to T_m was observed for the crystallization temperatures (T_c). Both T_m and T_c decrease with increasing styrene incorporation.

Tab. 2 shows the results of the copolymerization of ethylene and styrene performed at 60 °C and an ethylene pressure of 1 atm varying the styrene concentrations. Catalyst activity decreased with increasing styrene concentration. This is consistent with the observations for other catalytic systems[5, 16] used in the ethylene/styrene copoly-

merization, and can be explained by the much slower insertion rate of styrene with respect to ethylene. Initially the fraction of E−S copolymer increased, but decreased at high concentrations of styrene (Run 10). On the contrary, the fraction of sPS homopolymer increased with increasing styrene concentration. However, the amounts of the E−S copolymer and sPS homopolymer are low, with a maximum value of 5.3 and 6.5%, respectively. For comparison, the amounts of PE homopolymer was about 90%. This means, that the present catalyst system, CpTiCl₃/MgCl₂, favors the production of PE homopolymer, as described in a previous report[17].

In contrast to the heterogeneous CpTiCl₃/MgCl₂-PMAO catalyst, homogeneous CpTiCl₃-PMAO catalyst

produced only a mixture of syndiotactic poly(styrene) and poly(ethylene) without the formation of E–S copolymer, as shown in Tab. 2 (Run 11) and Fig. 1(c). This is consistent with the result of Aaltonen et al.[7] Based on this result, it is confirmed that E–S copolymers are produced from the heterogeneous phase of the active species of the CpTiCl$_3$/MgCl$_2$ catalyst.

On the other hand, with polydispersities of 3.8 to 4.5, the molecular weight distributions of E–S copolymers were significantly broadened in comparison to those typical for homogeneous metallocene-catalyzed ethylene/styrene copolymerizations[5,13,15], as shown in Tab. 2. A larger polydispersity is also accompanied by inhomogeneity of the active species with respect to styrene incorporation.

Styrene incorporation in the E–S copolymer also increased progressively with the increase of styrene concentration; with the styrene concentrations varying between 0.79 and 2.91 mol/L, the styrene contents varied between 3.9 and 9.0 mol-%, as shown in Tab. 2. These amounts of styrene incorporations are much higher than those obtained when using conventional Ziegler-Natta catalysts[1,2]. In addition, irrespective of the styrene content in the copolymer, all ^{13}C NMR spectra of the E–S copolymers gave only four resonance peaks observed at around 46.5, 37.2, 29.9, and 27.9 ppm. These resonances were assigned to $T_{\delta\delta}$, $S_{\alpha\delta}$, $S_{\delta\delta}$, and $S_{\beta\delta}$, respectively, as shown in Fig. 1(a). The absence of signals for $S_{\alpha\beta}$ and $S_{\beta\beta}$ at around 34.4 and 25.4 ppm indicates that a pseudorandom E–S copolymer is present instead of an alternating type, in contrast to other reports[9,10,12,14].

In conclusion, the copolymerization of ethylene and styrene using a MgCl$_2$-supported CpTiCl$_3$ catalyst resulted in copolymers containing long ethylene sequences and isolated styrene units. The production of the E–S copolymers were accompanied by the production of sPS and homo PE depending on the polymerization conditions. It is expected that ethylene-based styrene copolymers, especially in a slurry process, are obtained when using the present MgCl$_2$-supported metallocene catalyst.

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