

Low Dielectric Loss Polyethylene Polymerized with Chromocene Catalyst

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ABSTRACT: We studied the polymerization of ethylene monomers with chromocene catalyst to produce polyethylene with low dielectric loss in the microwave region. Chromocene (bis-cyclopentadienyl chromium) is very active for a long period during ethylene polymerization, and it also has a very low dipole moment because of its symmetrical molecular structure. Polyethylene polymerized by using chromocene has a low dielectric loss in the 500 MHz region caused by γ relaxation. We were able to calculate the loss in this wavelength region from a summation of each individual contribution. The contributors included catalyst residue, and polar groups, i.e., methyl groups and double bonds such as vinyl, internal *trans*-vinylene, and vinylidene groups at a certain crystallinity. In order to make low dielectric loss polyethylene with a chromocene catalyst, we first tried to improve both the process of ethylene polymerization with a chromocene catalyst and the dielectric loss ($\tan \delta$) of polyethylene at 500 MHz. We measured the number of polar groups and the residual catalyst in polyethylene with the IR method. Our results revealed that both the hydrogenation reaction that occurs during ethylene polymerization with the chromocene catalyst and the crystallization of polyethylene after polymerization were very effective in reducing the dielectric loss of polyethylene. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 441–448, 1998

Keywords: chromocene; polymerization; polyethylene; dielectric loss; hydrogen

INTRODUCTION

Polyethylene with low dielectric loss in the microwave region is an important material for use in producing submarine coaxial cable operating in the submillimeter wavelength region.¹ One of the basic criteria for polymers with low dielectric loss is that the constituent atoms in the polymer chains are linked with covalent bonds having very little dipole moment or having a small number of polar groups. These polyolefine polymers are only composed of carbon and hydrogen atoms. We have

already studied low dielectric loss polyethylene and how to reduce this loss even further.^{2,3}

We also studied the polymerization of ethylene with the Ziegler–Natta catalyst.⁴ From the results we found that the catalyst residue had a large dielectric loss and that the chemical formula of the residual catalyst in polyethylene particles changed over time; therefore, the dielectric loss of the polyethylene did not remain at a constant value. In this article we describe the process of ethylene polymerization with the chromocene catalyst. The chromocene was supported by silica particles. We used a chromocene catalyst to produce polyethylene with a low dielectric loss at 500 MHz because it has a symmetrical molecular conformation and because we believed that it would

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remain chemical stability during ethylene polymerization.

EXPERIMENTAL

Polymerization Catalyst

The chromocene (bis-cyclopentadienyl chromium) reagent we used was a 10 wt % toluene solution of chromocene manufactured by α -Products (USA). This 10 wt % solution was diluted to the desired concentration by adding toluene in a dry box in an Ar atmosphere. The chromocene was supported on silica particles (diameter: about 100 μm) whose average specific surface area was 150 m^2/g and the apparent density of the silica particles was 0.50 g/cm^3 (N608, Nikki Chemical). We prepared the polymerization catalyst as follows: The silica particles were heated in flowing Ar gas for 4 h at 500°C in an electric furnace to remove adsorbed water and oxygen gas. The silica particles were then removed from the furnace and introduced quickly into an autoclave, which was evacuated to about 3×10^{-3} Torr at 130°C for several hours. After we had cooled the autoclave to room temperature, we introduced a certain amount of chromocene solution under pressure using argon gas. The silica particles and chromocene solution were stirred for 30 min to support the chromocene on the particles.

Polymerization

A predetermined amount of ethylene was measured through a mass flow meter (maximum flow rate: 3 L/min, Ueshima-Brooks) and introduced into an autoclave reactor (volume: 300 mL) that was maintained at liquid nitrogen temperature (-195.8°C). Hydrogen gas was introduced into the autoclave immediately after the ethylene. The ethylene temperature was raised in two stages over a period of about 30 min. First, the autoclave was raised to room temperature by spraying it with tap water, then it was raised to 90°C in an electric furnace. After a certain period, the ethylene polymerization was stopped by releasing ethylene gas from the autoclave, which was then evacuated with a rotary vacuum pump at the polymerization temperature for several hours to eliminate toluene, cyclopentadiene, and residual ethylene monomer.

Hot Pressing Conditions and Polar Groups, Density, and Dielectric loss ($\tan \delta$) Measurements

The film specimens (300 μm thick) that we used for the $\tan \delta$ measurements were obtained by hot

pressing polyethylene particles immediately after polymerization. First, the particles were placed between metal plates and the temperature was raised to 180°C. Slight pressure was then applied to the particles to release gas, followed by hot pressing at 140 kg/cm^2 for 1 min. Then the polyethylene film between the two plates was rapidly cooled with running tap water from 180°C to about 20°C in 5 min. In another experiment we cooled the polyethylene film slowly. The cooling rate was controlled from 180 to 100°C for 24 h at 10^{-5} Torr and then the pressing temperature decreased spontaneously to room temperature. The numbers of functional groups in polyethylene were measured by using the absorbances of terminal vinyl ($-\text{CH}=\text{CH}_2$) at 909 cm^{-1} , vinylidene ($\diagup\text{C}=\text{CH}_2$) at 888 cm^{-1} , internal *trans*-vinylene ($-\text{CH}=\text{CH}-$) at 965 cm^{-1} , carbonyl at 1720 cm^{-1} , and aldehyde at 1733 cm^{-1} with an infrared spectrometer (Shimadzu model:IR-27G) using the baseline method. We measured the polyethylene density with the density gradient column method at 23°C and the average dielectric loss ($\tan \delta$) at 500 MHz calculated from three specimen measurements.

RESULTS AND DISCUSSION

Polymerization with a Chromocene Catalyst

Table I shows the maximum ethylene pressure and temperature of the five ethylene feeds. In the first and second feeds, the ethylene polymerization rate was very high, and the polymerization occurred rapidly even during the increase from liquid N_2 temperature to room temperature, so the maximum ethylene pressure did not increase to 62 atm. The polymerization heat for the first ethylene feed seemed to be the largest of all during a given time, but the polymerization temperature did not reach maximum during the five feeds because the polymerization heat was used to raise the autoclave from -196°C to room temperature. Figure 1 shows the relation between polymerization time and polymerization rate. A plot of $\log t$ versus $\log v$ (v : polymerization rate) gives a straight line over a long period of about 20 h. Enclosing the catalytic site with polyethylene particles while increasing the polymerization time may result in a reduction in the polymerization rate as the number of ethylene feeds is increased. The data follow eq. (1):

Table I Maximum Ethylene Pressure and Temperature of Five Ethylene Feeds during the Course of Polymerization

Ethylene Feed	Maximum Ethylene Pressure (atm)	Time (min)	Temperature (°C)	Maximum Temperature (°C)	Time (min)	Total Polymerization Time	Polymerization Rate (g/min)
1	62	9	50	98	28	32m	4.30
2	65	10	50	107	35	35m	1.03
3	81	29	80	114	50	11h25m	0.16
4	79	57	96	95	49	17h20m	0.0092
5	135	75	95	95	75	19h20m	0.0056

Catalyst composition: 0.224 g silica + 30 mg chromocene. Polymerization temperature: 90°C.

$$\log \nu = -1.19 \log t + 1.86 \quad (1)$$

where ν indicates the polymerization rate in g/min and t is polymerization time in min.

We found the possible reasons for the decreasing polymerization rate. One is a reduction in the possibility of contact between the propagation sites and the ethylene monomers, and the other is the deactivation of the active catalytic sites as the result of oxygen or water molecule contamination. We assumed the former reason to be predominant because the lifetime of this polymerization catalyst seemed to be very long. The concentration of the oxygen gas in the ethylene was about 5 ppm. If the polyethylene yield were 100 g, the amount of oxygen gas coexisting in the ethylene monomer would have

a calculated value of 5×10^{-4} g (i.e., 1.56×10^{-5} mol). This weight of oxygen gas corresponded to 9.6 mol % of chromocene, when we used 30 mg of chromocene. The amount of inactive chromocene catalyst seemed to be of almost the same order as the mol weight of oxygen gas. The mechanism by which the catalyst was made inactive by water was unclear, but the fractions of deactivated catalyst may be very small based on the ethylene polymerization steps and the long lifetime of the chromocene catalyst. To make polyethylene with lower dielectric loss, we should use a larger volume autoclave to avoid the polymerization rate decreasing along with the reaction time.

Table II shows polyethylene yields, densities, numbers of polar groups, and dielectric losses. The polyethylene density with chromocene catalyst was between 0.932 and 0.941. The polar groups in the polyethylene were methyl and double bonds such as vinyl, vinylidene, or vinylene groups. No hydroxyl or carbonyl groups were detected by infrared spectrum measurement. Methyl groups reduce the dielectric loss of polyethylene. This is because the methyl group has a lower dipole moment (0.1 Debye) than the vinyl group (about 3.5 Debye).⁵ The number of terminal double bonds was almost the same as those obtained with the Middle Pressure or Ziegler-Natta methods.

Figure 2 shows the relation between polyethylene yield and methyl group concentration per 1000 carbon atoms. The polyethylene yield increased as the methyl groups concentration decreased. We speculate that the degree of polymerization increased as the polymerization time increased, because the chromocene catalytic sites had a long lifetime of activity. If the above estimation were true, the molecular weight of polyethylene in the latter stage of polymerization

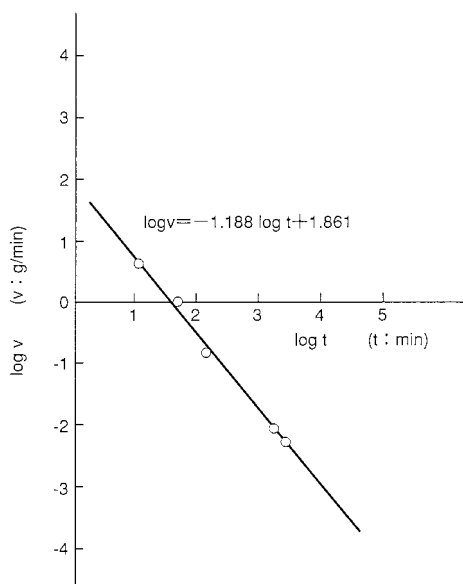


Figure 1 Relation between polymerization time and polymerization rate.

Table II Polyethylene Yields, Densities, Catalyst Content, Catalyst Composition, Numbers of Polar Groups and Dielectric Losses

No.	Name	PE Yield (g)	Density (g/cm ³)	Catalyst Content (wt %)	Weight (mg) of Chromocene/Silica	Numbers of Polar Groups/1000 Carbons						
						Methyl	Vinyl	Trans-Vinylene	Vinylidene	Total Unsaturation/1000C	Ratio (Int. trans/Vinyl)	Tan δ (μ rad)
1	π C-1	145.2	0.935	0.175	30/224	6.1	0.414	0.819	0.044	1.277	1.98	84
2	π C-3	65.8	0.932	0.386	30/224	6.3	0.598	0.639	0.031	1.268	1.07	98
3	π C-2	39.9	0.938	0.636	30/224	10.2	0.989	1.175	0.075	2.242	1.19	120
4	π C-5	26.8	0.934	0.945	30/224	12.4	1.085	1.152	0.061	2.298	1.06	141
5	π C-6	29.3	0.941	0.816	15/224	18.9	0.913	1.350	0.055	2.321	1.48	113
6	π C-7	28.5	0.933	0.806	6/224	n.d.	0.132	0.059	0.051	0.242	0.45	110
7 ^a	π C-8	62.5	0.956	0.407	30/224	6.4	0.158	0.062	0.103	0.323	0.39	49
8 ^a	π C-11	93.5	0.956	0.136	15/224	2.9	0.076	0.041	0.062	0.179	0.54	44
9	π C-12	96.8	0.927	0.085	10/74	n.d.	0.022	0.016	0.005	0.043	0.73	68
10	π C-13	111.7	0.926	0.057	7.5/56	0.2	0.188	0.222	0.010	0.042	1.18	70

Polymerization temperature: 90°C.

^a Hydrogen gas of 10 atm added.

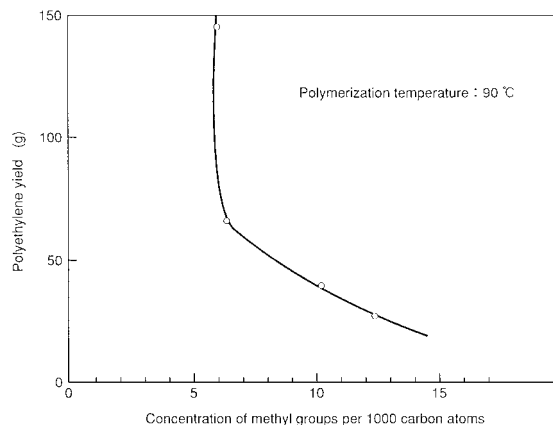


Figure 2 Relation between polyethylene yield and methyl group concentration per 1000 carbon atoms.

would be larger than that in the initial stage. But we have not yet measured the molecular weight of chromocene polyethylene with Gel Permeation Chromatography (GPC).

Dielectric Loss ($\tan \delta$) of Chromocene Polyethylene

Figure 3 shows the relation between chromocene catalyst content and dielectric loss at 500 MHz. The dielectric losses were measured for various polyethylene yields at a constant chromocene cat-

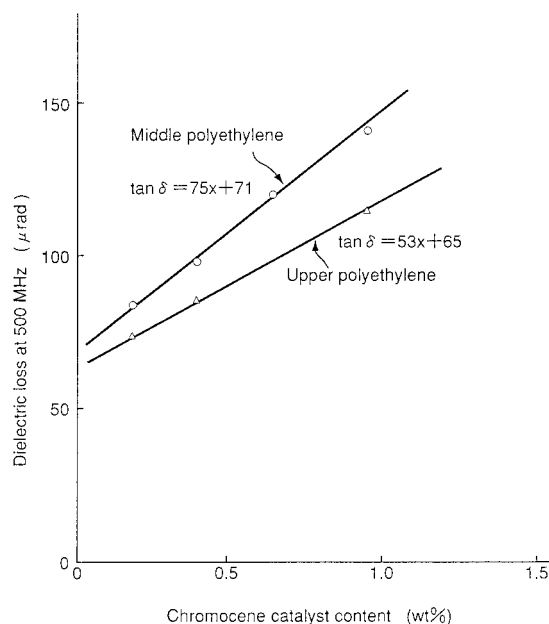


Figure 3 Relation between the chromocene catalyst content and dielectric loss. Middle polyethylene was collected from the middle part of the autoclave, and upper polyethylene was collected from the upper part.

alyst weight of 254 mg. The weight ratio of chromocene to silica was 0.134. The dielectric losses of polyethylene increased linearly with increases in chromocene catalyst content. The loss increment of the catalyst was about $75 \mu\text{rad}$ per 1 wt % of polyethylene. The dielectric loss values changed in relation to the sampling position in the autoclave. The measured dielectric loss of the upper part of the polyethylene was smaller than that of the middle part of the autoclave. The difference in dielectric loss was $10 \mu\text{rad}$ at 500 MHz with a chromocene catalyst content of 0.18 wt %. To reduce the variations in the dielectric loss of polyethylene with the sampling position, we have to fulfil the following two conditions. The first is that the polyethylene yields should be increased as much as possible, and the second is that the deactivation of the chromocene catalyst must be suppressed during the process of chromocene catalyst preparation. To increase catalyst activity, we should use newly developed equipment to introduce silica particles into a polymerization reactor in a vacuum. The data followed two straight lines given by eqs. (2) and (3) by using the least-squares method.

Dielectric losses of middle polyethylene:

$$\tan \delta = 75x + 71 \quad (2)$$

Dielectric losses of upper polyethylene:

$$\tan \delta = 53x + 65 \quad (3)$$

where x is the catalyst content (wt %), and $\tan \delta$ is the dielectric loss at 500 MHz (μrad).

The upper part of the polyethylene contained less chromocene catalyst than the middle part of the polyethylene. A silica catalyst content of 0.1 wt % or greater could be measured from infrared spectra by using the absorbance of the 480 cm^{-1} peak, which is assigned to the rocking vibration of Si—O—Si bonds. Figure 4 shows the relation between the chromocene catalyst content and absorbance at the 460 cm^{-1} peak. The relation is represented by eq. (4).

$$K = 12.1x \quad (4)$$

where K is the absorbance of the peak at 460 cm^{-1} obtained by the baseline method and x is the chromocene catalyst content (wt %).

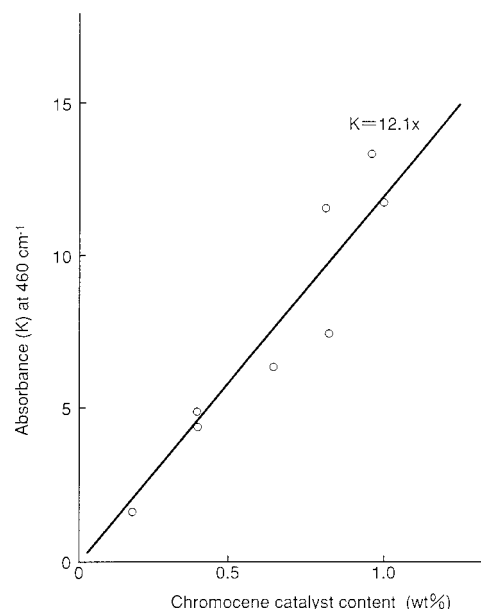


Figure 4 Relation between the chromocene catalyst content and absorbance at the 460 cm^{-1} peak.

Dielectric Loss of Residual Chromocene Catalyst

Table II shows the polyethylene yields, densities, catalyst content, catalyst composition, numbers of polar groups, and dielectric losses. To estimate the contribution of residual catalyst to dielectric losses, we measured the dielectric loss ($\tan \delta$) variations against the catalyst content.

The polyethylene densities with chromocene catalyst were $0.932\text{--}0.941 \text{ g/cm}^3$ for polymerization without the addition of hydrogen. They were smaller than the densities of Ziegler–Natta catalyzed polyethylene (its density is about 0.960 g/cm^3) and of polyethylene (its density is about 0.948 g/cm^3) made using the medium-pressure polymerization process (industrial processes were developed by Philips Petroleum Co. and Standard Oil Co. of Indiana).

Figure 5 shows the relation between chromocene weight at 0.224 g of silica and dielectric loss. The dielectric losses increased linearly with the increase in chromocene weight. The relation obeyed eq. (5):

$$\tan \delta = 1.76x + 87 \quad (5)$$

where x was the weight (mg) of the chromocene. The dielectric loss with only silica was estimated to be $87 \mu\text{rad}$ from eq. (5). The dielectric loss of bulk polyethylene was estimated to be $65 \mu\text{rad}$ from Figure 3. The difference of $22 \mu\text{rad}$ was

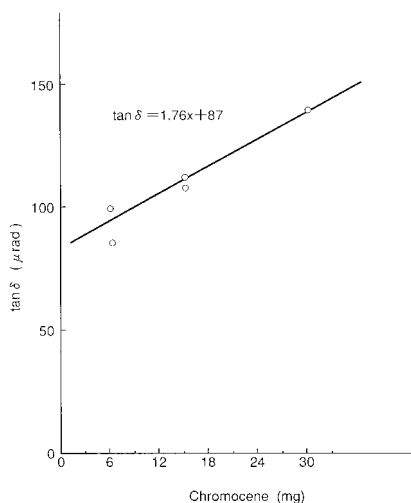


Figure 5 Relation between chromocene weight at 0.224 g of silica weight and dielectric loss.

attributed to the dielectric loss of 0.224 g of silica. We can conclude from the dielectric loss increments for 1 g of silica (98 μrad) and 1 g of chromocene (1760 μrad) that the dielectric loss increment of chromocene was 18 times that of silica. This fact indicates that the weight ratios of chromocene to silica must be designed to be as small as possible to produce low dielectric loss polyethylene in the microwave region. One of the criteria may be attained by using a vacuum apparatus to introduce the silica into the autoclave reactor and by using the reagents with higher catalytic activity of chromocene and silica. Furthermore, we must improve chromocene purity to prepare a more active chromocene catalyst for ethylene polymerization.

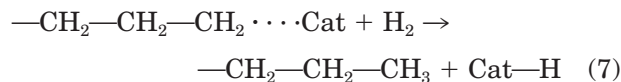
Hydrogen Gas Addition Polymerization and Crystallization of Ethylene

To reduce the dielectric loss of polyethylene, we looked at how to reduce the number of polar groups and how to make polyethylene with chromocene catalyst crystallize. We considered that eliminating any deactivation processes during the manufacture of the chromocene catalyst and increasing the catalytic activity of chromocene catalyst would be very effective ways to obtain low dielectric loss polyethylene. We obtained the lowest residual catalyst content of 0.0057 wt % (equivalent to a dielectric loss of 4.3 μrad at 500 MHz) in polyethylene ($\pi\text{C-13}$ in Table II, $\pi\text{C-#}$ indicates the number of the specimen in our study) with the chromocene catalyst. The contri-

bution to the dielectric loss by the residual catalyst of 5 μrad was negligible. Chromocene supported on silica is insoluble in toluene. This meant that the catalytic sites for the chromocene had many different chemical conformations in hetero phases for ethylene polymerization compared to a soluble catalyst such as metallocene catalyst used for the polymerization of propylene.⁶

On the other hand, to reduce the number of polar groups in polyethylene it is advantageous to produce monodispersed polyethylene, and the formation of polar groups in polyethylene must be suppressed. The use of a chromocene catalyst supported on silica was disadvantageous in terms of obtaining monodispersed polyethylene because there were many chemically heterogeneous chromocene catalytic sites.

Runs number 7 ($\pi\text{C-8}$) and 8 ($\pi\text{C-11}$) in Table II were polymerization reactions in the presence of 10 atm of hydrogen gas. Number 7 ($\pi\text{C-8}$) had almost the same polymerization conditions as those of number 2 ($\pi\text{C-3}$) except the coexistence of hydrogen gas with ethylene. The aim of adding hydrogen gas was to suppress the formation of terminal double-bond groups following the reaction in eq. (7).



The terminal double-bond formation was suppressed and the terminal methyl group formation became predominant. On the basis of the small values of the ratios of internal *trans*-vinylene to terminal vinyl for $\pi\text{C-8}$ and $\pi\text{C-11}$, hydrogen gas may suppress the formation of internal *trans*-vinylene groups. The polyethylene yields of runs $\pi\text{C-3}$ and $\pi\text{C-8}$ were almost the same, so the catalyst contents of the two were nearly equal. The polymerization conditions of the two reactions were almost the same except for the addition of hydrogen gas. The number of terminal vinyl was reduced to 1/3.8 from 0.598 to 0.158 per 1000 carbons and the number was reduced to 1/10.3 from 0.639 to 0.062 for internal *trans*-vinyl, but the number of vinylidene was increased from 0.031 ($\pi\text{C-3}$) to 0.103 ($\pi\text{C-8}$) per 1000 carbons. The total number of these unsaturation groups was reduced from 1.27 ($\pi\text{C-3}$) to 0.32 ($\pi\text{C-8}$) per 1000 carbons. The polyethylene density was increased from 0.932 ($\pi\text{C-3}$) to 0.956 ($\pi\text{C-8}$). The increase in the polyethylene density by hydrogen

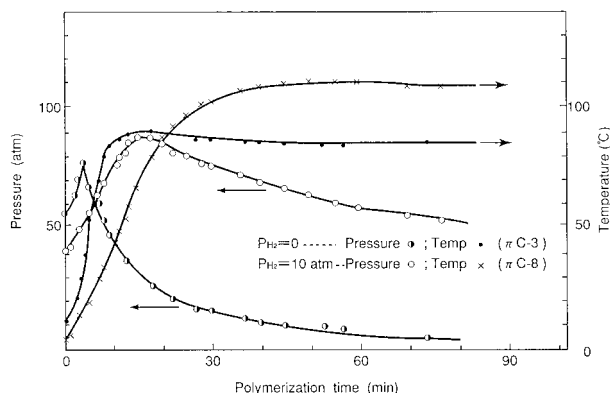


Figure 6 Pressure and temperature variations with nonhydrogen gas addition polymerization ($\pi C-3$) and hydrogen gas addition polymerization ($\pi C-8$) against polymerization time.

addition polymerization may be caused by the reduction in the number of unsaturated groups in the polyethylene. Run 8 ($\pi C-11$) in Table II was conducted with the addition of 10 atm hydrogen and catalyzed by 15 mg of chromocene to 0.224 g silica. The dielectric loss of $\pi C-11$ had the lowest value of 44 μrad in Table II. We believe that it exhibited the lowest dielectric loss because it had few unsaturated groups and because polyethylene has a relatively high density of 0.956. An important characteristic of the hydrogen addition polymerization was the increase in polyethylene density compared with the densities of 0.93–0.94 g/cm^3 without hydrogen addition polymerization. For polyethylene, produced without hydrogen being added during polymerization, the dielectric losses were not low at 110–113 μrad ($\pi C-6$, $\pi C-7$). Under the same polymerization conditions, the dielectric loss became lower as the polyethylene yield increases ($\pi C-1$ – $\pi C-3$, $\pi C-5$). Polyethylene of $\pi C-12$ and $\pi C-13$ had the lowest levels of residual chromocene catalyst of 0.085 and 0.057 wt %, but their dielectric losses (68 and 70 μrad) were not the lowest. These higher dielectric losses

may be caused by the fact that the polyethylene densities were comparatively low, for example 0.927 and 0.926.

Figure 6 shows pressure and temperature variations for polymerization with and without hydrogen gas, against polymerization time. The polymerization rate was reduced greatly by the addition of hydrogen gas. With $\pi C-3$, a maximum pressure of 78 atm was obtained 4 min after polymerization initiation. With $\pi C-8$, a maximum pressure of 89 atm was realized after 15 min. At 70 min after the initiation, the pressure difference of the two polymerization reactions was 50 atm. The difference between the dielectric losses of $\pi C-3$ and $\mu C-8$ was mainly caused by the number of polar groups and their polyethylene crystallinity ratios. As it is considered that there are almost the same number of methyl group in $\pi C-3$ and $\pi C-8$, a possible reason for the difference in $\tan \delta$ may be the difference in the number of double bonds.

Table III shows the cooling conditions, dielectric loss ($\tan \delta$) and density of polyethylene. Polyethylene $\pi C-11$ was produced by hydrogen gas addition polymerization, whereas $\pi C-12$ was produced without hydrogen gas.

The polyethylene density of $\pi C-11$ was greatly increased from 0.956 to 0.975 g/cm^3 by using a hot-press method with a prolonged cooling time. The dielectric loss of polyethylene $\pi C-11$ was reduced from 44 to 27 μrad . This dielectric loss of 27 μrad was the minimum value among all the polyethylene specimens. The reason may be that the amorphous region in polyethylene decreases when the slow cooling press is employed. On the other hand, the dielectric loss of $\pi C-12$ polyethylene was greatly reduced from 68 to 39 μrad , although the density increment was not as large, from 0.927 to 0.931 g/cm^3 in $\pi C-12$. The authors carefully prepared the specimens for the dielectric loss measurements by sampling from the center of the pressed polyethylene. This was to pre-

Table III Cooling Conditions, Dielectric Loss ($\text{Tan } \delta$), and Density of Polyethylene

Polyethylene	Dielectric Loss		
	Density		
		Rapid Cooling	Slow Cooling
$\pi C-11$	$\tan \delta$ (μrad)	44	27
	Density (g/cm^3)	0.956	0.975
$\pi C-12$	$\tan \delta$ (μrad)	68	39
	Density (g/cm^3)	0.927	0.931

vent the oxidation of the pressed polyethylene during the slow pressing process without the use of antioxidants.

CONCLUSIONS

We drew the following conclusions from our measurement of the polymerization of polyethylene with a chromocene catalyst supported on silica.

1. The polymerization catalyst consisting of chromocene supported on silica had a long lifetime of catalytic activity.
2. The numbers of polar groups such as vinyl and internal *trans*-vinylene groups and dielectric loss at 500 MHz were greatly reduced by the addition of hydrogen gas to the ethylene polymerization system with a chromocene catalyst supported on silica.
3. Chromocene supported on silica provided almost bulk polymerization containing only a very small amount of solvent as the chromocene reagent.
4. The addition of hydrogen gas to the polymerization system caused an increase in polyethylene density. The density of the polyethylene polymerized with a chromocene catalyst supported on silica was between 0.932 and 0.941.
5. An increase in polyethylene crystallinity

shown by the increase of density, caused a decrease in dielectric loss.

6. The smallest dielectric loss value was found in polyethylene produced by hydrogen gas addition polymerization catalyzed by chromocene supported on silica.

To apply this method for mass production, we must improve the chromocene catalytic activity to produce larger amounts of polyethylene per unit weight of the chromocene catalyst. For further study of the polymerization mechanism with a chromocene catalyst supported on silica, we must examine the degree of polymerization of the polyethylene with GPC.

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