Effects of Polymerization Conditions When Making Norbornene-Ethylene Copolymers Using the Metallocene Catalyst Ethylene Bis(indenyl) Zirconium Dichloride and MAO to Obtain High Glass Transition Temperatures

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ABSTRACT: Using 70 mol % norbornene in the monomer mixture before polymerization, the influences of different polymerization conditions were studied. It was found that by increasing the temperature from 10 to 70°C, the yield increased and the molecular weight decreased; and when increasing the ethylene pressure from 2 to 6 atm, yield and molecular weight increased. The highest glass transition temperatures, however, were achieved at 30°C and 4 atm. Further improvements could be obtained by increasing the amount of catalyst or Al/Zr ratio. Using the conditions of 30°C, 4 atm, 4 mg catalyst, 3000 Al/Zr, 250 mL toluene solution, and 30 min, the amount of norbornene was increased from 31.1 to 90 g, resulting in an increase in the glass transition temperature from 98 to 155°C. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1063–1070, 1997

INTRODUCTION

By incorporating rigid cyclic monomers in a polymer chain, increased glass transition temperatures and hence improved heat resistance can be obtained. Such heat resistant polymers are already on the market, and they are made by metathesis ring-opening polymerization (Japan Synthetic Rubber's ARTON, Nippon Zeon's ZEONEX, and BF Goodrich's TELENE OP for optical applications, and many companies are developing or manufacturing elastomers and reaction injection molding (RIM) systems based on metathesis ring-opening polymerization) or vanadium catalyzed addition copolymerization with ethylene (Mitsui Sekka's APO and APEL). Because these polymers are amorphous and have very good optical proper-

ties, they are primarily used in optical applications such as laser disks where they compete with polycarbonate[1-5] (pers. commun. with representatives of Japan Synthetic Rubber, Nippon Zeon, and Mitsui Sekka.).

The metallocene catalyst technology developed by Sinn and Kaminsky for ethylene and propylene polymerization[6] was later also successfully employed by Kaminsky et al. in the homo- and copolymerization of cycloolefins.[7,8] These cycloolefins polymerized without ring opening occurring, and when copolymerized with ethylene or propylene low incorporations decreased the crystallinity until amorphous elastomeric copolymers were obtained. Higher incorporation of cycloolefins stiffened the polymer chain so that engineering plastic properties like a high glass transition temperature were obtained. Because metallocene catalyzed addition copolymerization with ethylene provides more options for tailormaking the properties of the copolymers, this field was investi-

gated and patented by Mitsui Sekka and Hoechst.[9-16] These two companies then started to work together on metallocene catalyzed cycloolefin copolymers (COC), with norbornene-ethylene copolymers as their first target. These norbornene-ethylene copolymers were recently introduced on the market under the tradenames APEL and TOPAS. They are expected to compete mainly with polycarbonate (PC), acrylonitrile-butadiene-styrene (ABS), and PC/ABS blends in technical, nonoptical applications[17] and with PC and other COCs in optical applications.[5,18] By using low amounts of norbornene, polymers with elastomeric properties can been obtained and this field was studied by Idemitsu Kosan Co., Ltd.[19]

The intention of this publication is to demonstrate the influences of the main parameters when copolymerizing norbornene and ethylene using ethylene bis(indenyl) zirconium dichloride as catalyst and methylaluminoxane (MAO) as cocatalyst. These main parameters are the norbornene content, the polymerization temperature, and the ethylene pressure. The influences of catalyst concentration, Al/Zr ratio, and polymerization time were also studied. The properties of interest were the norbornene content in the polymer and its influence on the glass transition temperature. The activity, the conversion of norbornene, and the molecular weight and its distribution were also measured.

EXPERIMENTAL

Apparatus and Polymerization Method

The copolymerization of norbornene and ethylene was done using a semiflow method and a reactor system described in detail in an earlier article by our group.[20] The appropriate amount of norbornene was dissolved in toluene and diluted so that a 250-mL solution was obtained. The solution was dried with molecular sieves overnight and poured into a thermostated 500-mL stainless steel reactor equipped with a stirrer. After purging with nitrogen and ethylene the ethylene pressure and the temperature of the reactor content were set at the chosen values and ethylene was supplied until the toluene solution was saturated and the ethylene flow stopped. Then the MAO-toluene solution was pumped into the reactor and the mixing continued for 15 min. Finally the catalyst-toluene solution was pumped to the reactor. After the addition of catalyst ($2 \text{ mg} = 19 \cdot 10^{-6} \text{ mol/L}$

or $4 \text{ mg} = 38 \cdot 10^{-6} \text{ mol/L}$) the polymerization was allowed to continue for 60 or 30 min, the ethylene consumed in the polymerization was constantly replaced, and the pressure and temperature were automatically controlled. No hydrogen or other chain transfer agents were used in this study. When the chosen polymerization time was finished the ethylene supply was shut off, the reactor vented, and the reactor content poured into ethanol (300 mL). Then hydrochloric acid was added to deactivate the MAO and the sample was kept that way until the next day when it was filtered, washed with acetone, filtered again, and dried in a vacuum oven.

Chemicals

The catalyst was the soluble metallocene catalyst ethylene bis(indenyl) zirconium dichloride, EURECEN 5036, and the cocatalyst was 10 wt % MAO in toluene, both from Witco. The Al content of the cocatalyst was 4.5–5.5 wt %.

The comonomer, norbornene (bicyclo 2.2.1.hept-2-ene), was obtained from Fluka (14351); its purity was 97%.

The ethylene used was AGA's grade 2.7, which was further purified in columns containing molecular sieves, CuO, and Al_2O_3 before entering the reactor. Riedel-de-Häen's grade RG toluene was used.

Polymer Characterization

The glass transition temperatures (T_g) and melt temperatures (T_m) were measured using Perkin–Elmer's DSC 7 so that the sample was first heated to 200°C, then cooled to 0°C (20°C/min), and after that heated again to 200°C (10°C/min). The data used in this publication were taken from the second heating.

The weight average molecular weights ($\bar{M}_w$), number average molecular weights ($\bar{M}_n$), and the molecular weight distributions ($\bar{M}_w/\bar{M}_n$) were measured by GPC. The equipment used was a Waters 150 ALC equipped with three (Polymer Laboratories) columns (10^3, 10^5, 10^6 Å) and 1,2,4-trichlorobenzene as solvent. The temperature was 140°C and the flow rate 1 mL/min. Because the columns were calibrated universally with narrow molecular weight polystyrenes, the results are not absolute but relative.

The norbornene content in the polymer was measured by integrating the signal obtained from the GPC (V·s) and dividing by the weight of the sample (mg). The higher the norbornene content

Table I   Ethylene Dissolved in Toluene (mol/L) at Different Ethylene Pressures and Temperatures

Pressure (atm)	Temperature (°C)			
	10	30	50	70
2	0.374	0.266	0.195	0.143
4	0.761	0.544	0.405	0.310
6	1.159	0.825	0.618	0.477

in the polymer, the smaller the difference in refractive index between the polymer solution and the pure solvent and the lower the V·s/mg value. At 29 mol % norbornene no GPC curve was obtained, and at higher norbornene contents the polarity of the signal was reversed. The GPC results for norbornene-ethylene copolymers with norbornene contents close to 29 mol % are, therefore, very inaccurate due to the very weak signal. By using a calibration curve established by plotting the norbornene contents obtained from ^{13}C-NMR spectroscopy versus the above mentioned V·s/mg values, the results can be reported in mol percent norbornene. This recently developed analytical method will be published in a separate article. The ^{13}C-NMR data used for this calibration curve were obtained from a 400-MHz Jeol NMR spectrometer, which was used at 110–130°C with 1,1,2,2-tetrachloroethane as solvent.

RESULTS AND DISCUSSION

To find the most suitable polymerization temperature and ethylene pressure for norbornene-ethylene copolymers, four temperatures (10, 30, 50, and 70°C) and three ethylene pressures (2, 4, and 6 atm) were investigated for an initial norbornene concentration of 70 mol %. The amount of ethylene in mols/liter dissolved in toluene at the temperatures and pressures mentioned above are presented in Table I, which is based on Henry's law and provided by the Borealis Company. Based on this data and assuming that the solubility of ethylene in diluted solutions is approximately the same as in the pure solvent, the amount of norbornene representing 70 mol % could be calculated for each combination of temperature and pressure. To obtain enough copolymer at all conditions the rather long 1-h polymerization time as well as the rather high 3000 Al/Zr ratio were used.[20-22]

The polymerization conditions and the results for this experiment are presented in Table II.

Molecular Weights and Activities

It can be seen from the results presented in Table II that the higher the ethylene pressure, the higher the molecular weights due to higher total monomer concentrations that have an increasing effect on the propagation reaction in relation to the termination and chain transfer reactions.[21] However, the activities calculated per atmosphere ethylene were on the same level regardless of the ethylene pressure. At lower polymerization temperatures higher molecular weights were obtained for all pressure levels because of less chain transfer reactions in relation to the propagation reaction.[23] Cherdron et al. also reported that norbornene-ethylene copolymers form quasiliving polymers, which would also increase the molecular weights for lower temperatures.[18] Contrary to their experience, however, the molecular weight distributions decreased with increasing temperatures (and pressures). This discrepancy is probably due to different polymerization procedures. In this investigation the polymerization of ethylene increased with increasing temperature and pressure, providing a narrower molecular weight distribution. At the lowest temperature, 10°C, the activities were, however, so low that this temperature will not be used in further experiments on norbornene-ethylene copolymers. When increasing the temperature from 10 to 30°C, there was a significant increase in yield whereas a further increase in temperature to 50°C had only a slight effect. This might be due to an increasing effect on reactivity in combination with a decreasing effect on ethylene solubility causing lower concentrations of both monomers. The polymerizations made at 2 atm are less reliable than the other two pressure levels because of the bigger relative error in the pressure control.

Norbornene Content in Polymer and Its Glass Transition Temperature

When increasing the polymerization temperature the norbornene content decreased for all pressure levels due to an increasing relative reactivity of ethylene.[23] It can also be seen that the highest levels of norbornene contents and glass transition temperatures were achieved when using the ethylene pressure of 4 atm with the highest glass transition tem-

Table II Influence of Ethylene Pressure and Polymerization Temperature on Norbornene-Ethylene Copolymers

Run	Pressure (atm)	Temp. (°C)	Yield (g)	Activity (10^6 g/mol Zr h atm)	GPC Data				T_g (°C)	Conversion of Norbornene (%)
					$\bar{M}_w$ (10^3 g/mol)	$\bar{M}_n$ (10^3 g/mol)	$\bar{M}_w/\bar{M}_n$	Norbornene (mol %)		
1	2	10	2.2	0.2	—	—	—	29	82	6
2	2	30	3.0	0.3	188	67	2.8	24	47	11
3	2	50	2.2	0.2	98	48	2.1	21	<0	9
4	2	70	15.0	1.6	48	19	2.5	16	<0	71
5	4	10	6.9	0.4	—	—	—	29	76	10
6	4	30	22.3	1.2	228	108	2.1	30	90	43
7	4	50	23.5	1.2	—	—	—	29	85	58
8	4	70	38.4	2.0	71	42	1.7	25	<0	100
9	6	10	14.6	0.5	368	250	1.5	28	67	12
10	6	30	22.4	0.8	—	—	—	29	77	28
11	6	50	29.2	1.0	202	144	1.4	32	86	50
12	6	70	31.7	1.1	148	125	1.2	28	<0	69

Copolymers were polymerized for 1 h starting from 70 mol % norbornene, $19 \cdot 10^{-6}$ mol/L ethylene bis(indenyl) zirconium dichloride, and 3000 Al/Zr as MAO in toluene.

(—) No signal from the refractometer due to the same refractive index for the solution and the solvent.

peratures obtained for the polymerization temperatures 30 and 50°C. For 10°C lower values were obtained because of the lower conversion of norbornene and the higher solubility of ethylene. For 70°C, on the other hand, the relative reactivity of ethylene was so high that no glass transition temperature (below 0°C) was seen for 4 and 6 atm; and for 2 atm even a partly crystalline polymer with the melting point of 129°C was obtained.

At 6 atm the total monomer/catalyst ratio was higher than for 4 atm, which seems to have decreased the incorporation of norbornene and hence the glass transition temperature.

When taking all the above into consideration, the ethylene pressure of 4 atm and the polymerization temperature of 30°C was the most promising combination. Under these conditions the glass transition temperature was 90°C and the molecular weight as well as the activity were high. The norbornene content in the polymer was 30 mol %.

This work continued by further improving the heat resistance (glass transition temperature) of the norbornene-ethylene copolymer made at 4 atm and 30°C by looking for more favorable polymerization times, catalyst contents, and Al/Zr ratios and then systematically increasing the norbornene content from 31.1 (70 mol %) to 90 g.

Polymerization Time, Catalyst Content, and Al/Zr Ratio

From Table III can be seen that by decreasing the polymerization time from 1 h to 30 min, no increase in glass transition temperature was achieved, even if the average norbornene content in the reaction mixture must be higher for a shorter polymerization time. One explanation for this is that the ethylene content also decreased as the polymerization proceeded because the polymer/toluene solution is rather viscous and one could expect a decreased mass transfer of ethylene. The molecular weight distributions ($\bar{M}_w/\bar{M}_n$) obtained were, however, narrower for shorter polymerization times, which is consistent with Cherdron and colleagues' findings.[18] By increasing the amount of catalyst from 2 to 4 mg significant increases in yields, norbornene conversions, and glass transition temperatures were seen for all three ethylene pressure levels. This can be explained by the lower total monomer/catalyst ratios, which makes it easier for norbornene to reach an active center. At higher ethylene pressures the norbornene conversions as well as the glass transition temperatures were lower because of the higher concentrations of ethylene, which is less prone to mass transfer limitations than norbornene. In the region of 29 mol % norbornene incorporation, however, very different glass transition temperatures were obtained. The higher glass transition temperatures might have been due to stiffer norbornene-norbornene segments in the polymer chain. This is an area that would be a suitable topic for further investigations. At shorter polymerization times and lower ethylene pressures (lower total monomer concentrations)

Table III   Influence of Shorter Polymerization Time (30 min), Catalyst Content, and Al/Zr Ratio

Run	Pressure (atm)	Catalyst (10^{-6} mol/L)	Al/Zr	Yield (g)	Activity (10^6 g/mol Zr h atm)	GPC Data			Norbornene (mol %)	T_g (°C)	Conversion of Norbornene (%)
						$\bar{M}_w$ (10^3 g/mol)	$\bar{M}_n$ (10^3 g/mol)	$\bar{M}_w/\bar{M}_n$			
13	2	19	3000	9.5	2.0	—	—	—	29	86	36
14	4	19	3000	15.3	1.6	—	—	—	29	90	28
15	6	19	3000	10.9	0.8	—	—	—	29	74	14
16	2	38	3000	14.1	1.5	152	119	1.3	30	98	55
17	4	38	3000	17.3	0.9	—	—	—	29	101	32
18	6	38	3000	24.5	0.9	—	—	—	29	92	32
19	4	19	1500	10.5	1.1	—	—	—	29	84	20
20	4	19	6000	13.1	1.4	—	—	—	29	93	24

Values are when polymerizing norbornene-ethylene copolymers at 30°C starting from 70 mol % norbornene using ethylene bis(indenyl) zirconium dichloride and MAO in toluene.

(—) No signal from the refractometer due to the same refractive index for the solution and the solvent.

the activities as defined in this work were higher. The influence of Al/Zr ratio was in this stage studied only for the 4-atm ethylene pressure, and one can see that the higher the Al/Zr ratio the higher the glass transition temperature.[11] The difference between 6000 and 3000 Al/Zr was, however, so small that it was decided that mainly 3000 Al/Zr will be used when further investigating norbornene-ethylene copolymers.

Systematically Increased Norbornene Contents

Using the polymerization conditions of 30°C, 4 atm, 4 mg catalyst, 3000 Al/Zr, and 30 min, the amount of norbornene was increased from 31.1 (70 mol %) to 90 g. All the test results are presented in Table IV, and the glass transition temperatures are plotted in Figure 1. As a comparison equivalent data for 2 mg catalyst and 1500 and 6000 Al/Zr are presented in Table V. From Table IV and Figure 1 it can be seen that the higher the norbornene content in the polymerization mixture, the higher the norbornene content in the polymer and the higher the glass transition temperature.[23] The T_g values, however, increased more rapidly than the norbornene incorporation in the polymer indicating "block structures." This phenomenon will be presented more in detail in future publications. The conversion of norbornene, however, decreased with increasing norbornene content.[21] The yield also stayed on the same level for all norbornene contents except the highest one.[21] In Table V the increasing effect of catalyst content and Al/Zr ratio on the yield, norbornene content, and glass transition temperature is once again presented. For the highest norbornene content, 90 g, a low yield was obtained also for 1500 Al/Zr as was the case for 3000 Al/Zr. The glass transition temperatures were in most cases very difficult to distinguish and in a few cases they could not be seen at all. Therefore, the lack of a T_g value in Table V does not mean that the heat resistance would be low.

CONCLUSIONS

When copolymerizing norbornene and ethylene using the metallocene catalyst ethylene bis(indenyl) zirconium dichloride and MAO, we obtained very high incorporations of norbornene (38 mol %) in the polymer, which increased the glass transition temperature to 155°C. This provides an opportunity to manufacture heat resistant engi-

Table IV   Influence of Norbornene Content on Properties of Norbornene-Ethylene Copolymers

Run	Norbornene (g/250 mL)	Yield (g)	Activity (10^6 g/mol Zr h atm)	$\bar{M}_w$ (10^3 g/mol)	$\bar{M}_n$ (10^3 g/mol)	$\bar{M}_w/\bar{M}_n$	Norbornene (mol %)	T_g (°C)	Conversion of Norbornene (%)
					GPC Data				
17	31.1	17.3	0.9	—	—	—	29	101	32
21	40	14.2	0.8	290	163	1.8	33	122	22
22	50	11.0	0.6	361	223	1.6	34	124	14
23	60	13.7	0.7	378	197	1.9	36	136	15
24	70	15.5	0.8	406	282	1.4	34	142	14
25	80	13.3	0.7	446	268	1.7	36	147	11
26	90	3.5	0.2	269	206	1.3	38	155	3

Copolymers were polymerized at 4 atm ethylene pressure and 30°C for 30 min using $38 \cdot 10^{-6}$ mol/L ethylene bis(indenyl) zirconium dichloride and 3000 Al/Zr as MAO in toluene.

(—) No signal from the refractometer due to the same refractive index for the solution and the solvent.

neering plastics in a polyethylene or polypropylene plant and, therefore, has great commercial potential. The polymerizations presented in this publication were all homogenous, therefore requiring rather high catalyst and cocatalyst contents; and the norbornene contents needed were very high. All these matters are very critical from an economic point of view and should be optimized when scaling up the process. Also the type of solvent used and the separation and purification of the polymer need to be optimized. However, the basic properties and their dependence on the poly-
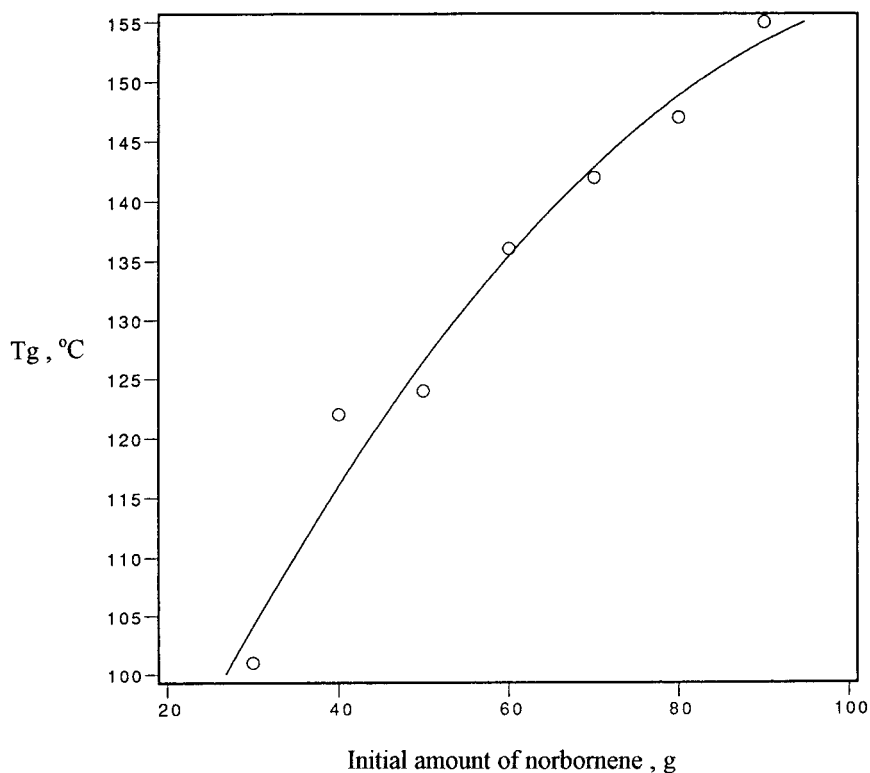

Figure 1   Influence of norbornene content on the properties of norbornene-ethylene copolymers polymerized at 4 atm ethylene pressure and 30°C for 30 min using $38 \cdot 10^{-6}$ mol/L ethylene bis(indenyl) zirconium dichloride and 3000 Al/Zr as MAO in toluene.

Table V Influence of Al/Zr Ratio and Catalyst Content on Properties of Norbornene-Ethylene Copolymers

| Run | Norbornene (g/250 mL) | Catalyst (10^{-6} mol/L) | Al/Zr | Yield (g) | Activity (10^6 g/mol Zr h atm) | GPC Data | | | | T_g (°C) | Conversion of Norbornene (%) |
						$\bar{M}_w$ (10^3 g/mol)	$\bar{M}_n$ (10^3 g/mol)	$\bar{M}_w/\bar{M}_n$	Norbornene (mol %)		
27	50	38	1500	13.1	0.7	482	318	1.5	33	116	16
28	50	38	6000	17.2	0.9	298	187	1.6	32	121	21
29	70	38	1500	17.8	0.9	484	281	1.7	33	122	16
30	70	38	6000	22.6	1.2	311	175	1.8	37	ND	21
31	90	38	1500	8.7	0.5	403	276	1.5	35	130	6
32	90	38	6000	21.7	1.1	351	212	1.7	37	ND	16
33	50	19	3000	9.1	1.0	515	335	1.5	31	104	11
34	70	19	3000	6.1	0.6	520	344	1.5	32	114	5
35	90	19	3000	3.9	0.4	413	264	1.6	33	123	3
36	90	19	1500	1.6	0.2	256	215	1.2	34	124	1
37	90	19	6000	3.3	0.3	352	218	1.6	34	117	2

Copolymers were polymerized at 4 atm ethylene pressure and 30°C for 30 min using high amounts of norbornene, ethylene bis(indenyl) zirconium dichloride as catalyst, and MAO as cocatalyst. ND, T_g could not be distinguished with the DSC method used.

merization conditions presented here can be expected to be useful as guidelines when scaling up a process for the manufacturing of norbornene-ethylene copolymers using ethylene bis(indenyl) zirconium dichloride as catalyst and, to a lesser extent, for related copolymers and metallocene catalysts. It can be seen that there is an optimum temperature and an optimum ethylene pressure that should be used in order to obtain high incorporations of a cyclic comonomer and increased glass transition temperatures and that these properties can be further increased by increasing the catalyst concentration, the Al/Zr ratio, and the comonomer content in the reaction mixture. Especially very low (10°C) or very high (70°C) polymerization temperatures should be avoided in future work. At low temperatures the activities and the comonomer incorporations are low and such conditions are also very impractical for present polyethylene and polypropylene reactors. On the other hand, at high temperatures the comonomer incorporation especially is much too low; and, depending on the other conditions, the molecular weights might also be too low. For each COC concept and manufacturing technology the optimization of the polymerization temperature is one of the most essential tasks. More detailed studies on norbornene-ethylene copolymers made under optimum conditions will be presented in future studies, and these will also include the appearance of block structures.

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