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Nickel (salen) / methylaluminoxane catalyzed polymerization of norbornene

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Summary

Nickel (salen) in conjunction with methylaluminoxane (MAO) catalyzes the polymerization of norbornene to poly (2,3-bicyclo [2.2.1] hept-2-ene) [poly (norbornene)]. Methylaluminoxane (MAO) was used as cocatalyst as such (MAO-I) and after distilling off free trimethylaluminium (MAO-II). The catalyst system was very active in chlorobenzene at room temperature. It was also found that MAO-II gave higher activity as compared to MAO-I. The samples of polynorbornene were soluble in 1,2,4-trichlorobenzene. The poly (norbornene)s were characterized by intrinsic viscosity and thermal properties.

Introduction

Norbornene can be polymerized by different ways depending upon the nature of catalyst. The metathesis polymerization of norbornene is well studied (1). Cationic polymerization of norbornene using ethyl aluminum dichloride leads to formation of poly (2,7 bicyclo [2,2,1] hept-2-ene) (2). The vinylic polymerization of norbornene without opening of the ring is of much importance, as it leads to high melting polymer, which is not soluble in common, hydrocarbon solvents (3). The polymerization of norbornene using vinylic unsaturation was also carried out using Pd (II) catalyst. While Schultz (4) and Kiennemann et al. (5) used $PdCl_2$ and $Pd(C_6H_5CN)_2Cl_2$ as catalyst respectively, Risse et al. (6,7) used cationic complexes of palladium for polymerization of norbornene. Heitz et al. (8,9) studied extensively the vinylic polymerization of norbornene using chromium and palladium based catalysts. Nickel based catalyst are also known for polymerization of norbornene. Goodall et al. (10) used nickel ethylhexanoate along with $HSbF_6$ for homopolymerization of norbornene. Arndt et al. (11) used Nickel (acetyl acetonate) along with MAO for the polymerization of norbornene. More recently, Greiner et al. (12) used nickel based phosphoraneiminato complexes along with MAO to obtain highly active catalyst for vinylic polymerization of norbornene.

In this paper we report the use of Ni (salen) in combination with MAO for the addition or vinyl type homopolymerization of norbornene resulting in poly (2,3-bicyclo [2,2,1] hept-2-ene) (PNB).

Experimental

All manipulation involving air sensitive compounds were carried out under a stream of dry nitrogen using standard bench top inert techniques.

Materials

Nickel acetate tetrahydrate, ethylene diamine and salicyaldehyde were obtained from Aldrich and used without any purification. Norbornene was distilled over calcium hydride. Norbornene (20.21 g) was made upto 100 mL using toluene or chlorobenzene (stock solution). Methylaluminoxane (MAO-I) was obtained from Witco, Germany as 30 % solution in toluene. Methylaluminoxane (10 mL) was subjected to vacuum distillation (25 °C, 0.1 mm Hg) to obtain 2.7 g of a glassy solid. This was dissolved in 10 mL toluene (MAO-II). The MAO-I and MAO-II were analyzed for aluminum content by EDTA titration. Methyl content was determined from the volume of methane gas evolved on reaction with 1-heptanol. Toluene (Loba chemicals, GR grade) was dried over sodium and distilled before use. Chlorobenzene (CB) was dried over calcium hydride and distilled under nitrogen.

Ni (Salen) was prepared from salicyaldehyde, ethylenediamine, and nickel(II)acetate tetrahydrate according to reported procedures (13)

Yield 80%; Elemental analysis, Observed C = 58.5 %; H = 4.2 %; N = 8.7 %. Theoretical C = 59 %; H = 4.3 %; N = 8.6 %.

Polymerization of Norbornene

The polymerization of norbornene was carried out as follows. In a three neck 25 mL round bottom flask, previously flushed with argon, 10 mL of a stock solution of norbornene in chlorobenzene containing 2.02 g (2.15×10^{-2} mol) norbornene was taken. The stirring was carried out using a magnetic needle. To this flask, MAO-II solution containing 2.15×10^{-3} mol of aluminum was added. This was followed by Ni (salen) solution containing 7 mg of Ni(salen) (2.15×10^{-5} mol.) in chlorobenzene. The solution became viscous within one minute. The whole mass was poured into 100 mL of acidified methanol. The precipitated polymer was filtered, washed with fresh methanol and dried in a vacuum oven at 80 °C for two hours.

Analysis of polymer

Infrared spectrum was recorded on Perkin Elmer PC 16 FTIR spectrometer (KBr pellet). ^{13}C NMR spectrum was recorded at room temperature on CP-MAS Bruker 300 MSL in the solid state. Viscosity measurements were carried out in 1,2,4 trichlorobenzene at 135 °C using ubbelohde viscometer. Thermogravimetric analysis and differential scanning calorimetric (DSC) measurements were carried out on Perkin Elmer DSC-7 instrument in a nitrogen flow with a heating rate of 10 °C /min.

Results and Discussion

Polymerization of norbornene was carried out under different reaction conditions, using MAO-I and MAO-II as cocatalysts (Table 1). Absence of cationic polymerization of norbornene was demonstrated using appropriate blank experiments (run. no's 1+5) Initial experiments were carried out in toluene (run no. 2-4) and low polymerization activities were obtained. The PNB also precipitated as the polymerization proceed. Deffieux et al. (14) obtained very active catalyst when Ni stearate was used along with MAO. They also observed precipitation of PNB during polymerization. However, high activities were noted when chlorobenzene was used which also acted as solvent for PNB. Therefore further experiments were carried out using chlorobenzene as solvent.

Effect of Type of MAO

The MAO obtained commercially from Witco (MAO-I) contains a higher amount of free TMA compared to MAO obtained after distilling (MAO-II) [MAO-I Me/Al 1.37 ; MAO-II Me/Al 1.16]. It was found that polymerization using MAO-II gave higher activities in comparison to MAO-I. MAO-I as cocatalyst at M/Ni 1000 and Al/Ni 100 gave an activity 227 kg/ mol Ni. h., whereas MAO-II gave an activity of 1120 kg/ mol Ni. h. [run no. 6 and 12). When monomer to Ni ratio was increased keeping other parameters constant, there was decrease in catalyst activities. The run carried out at higher M/Ni also showed much higher activities in case of MAO-II [run no. 7, 8, 13 and 14]

Table 1. Polymerization[a] of norbornene in the presence of Ni(salen)/MAO at 25°C

Run no.	Solvent	[CAT] mmol/lit	M/Ni mol/mol	MAO type	[Al] mmol /lit	Al/Ni mol/ mol	Time, min.	Yield %	Activity kg PNB/ mol. Ni h.	[η]* dl/g
1	TL	-	-	I	215	-	120	Traces	-	-
2	TL	4.3	500	I	64.5	15	30	11.3	10.6	
3	TL	2.15	1000	I	215	100	120	13.4	6.3	
4	TL	2.15	1000	II	215	100	120	29.3	13.8	
5	CB	-	-	II	215	-	120	Traces	-	
6	CB	2.15	1000	I	215	100	5	20.1	227	1.7
7	CB	0.43	5000	I	43	100	5	1.60	90.2	2.3
8	CB	0.215	10000	I	21.5	100	5	0.53	59.8	2.8
9	CB	2.15	1000	II	2.15	10	60	Traces	-	-
10	CB	2.15	1000	II	107.5	50	5	33.3	376	3.3
11	CB	2.15	1000	II	215	100	1	46.7	2634	3.1
12	CB	2.15	1000	II	215	100	5	99.3	1120	3.0
13	CB	0.43	5000	II	43	100	5	15.3	863	4.8
14	CB	0.215	10000	II	21.5	100	5	0.67	75.6	4.9
15	CB	0.108	20000	II	108	1000	1	9.5	10716	2.2
16	CB	0.108	20000	II	108	1000	5	29.6	6678	2.1

a) Polymerization condition 10 mL solution containing 2.15 X 10^{-2} mol of NB is used for each run.

b) Determined in 1, 2, 4 trichlorobenzene at 135 °C

Effect of Al/Ni ratio

The Al/Ni ratio were varied from 10 to 100 keeping M/Ni ratio constant [run no. 9-11). Whereas, only traces of polymer could be obtained at Al/Ni ratio 10, higher activity (376 kg PNB/ mol Ni. h) was obtained at Al/Ni 50. At Al/Ni ratio 100 (run no. 11) a large exotherm was observed and polymerization mass became highly viscous within one minute. Very high activity of 2634 kg PNB/mol Ni. h. was obtained with 47%

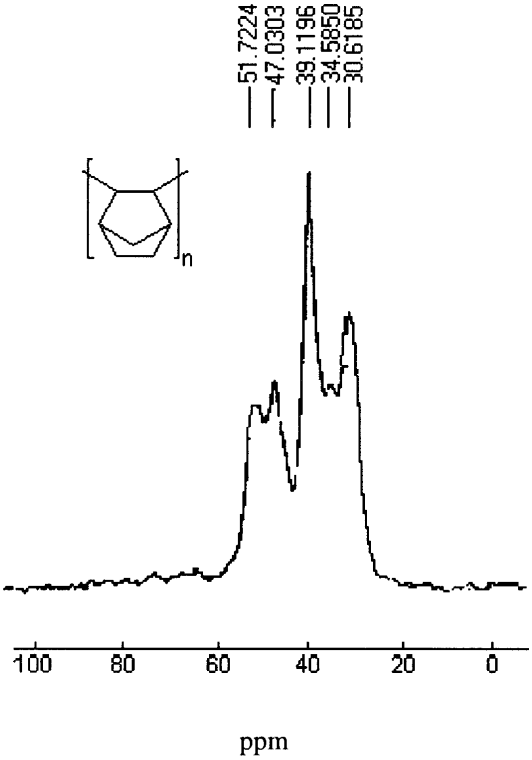


Figure 1. Solid state ^{13}C NMR spectrum of Polynorbornene

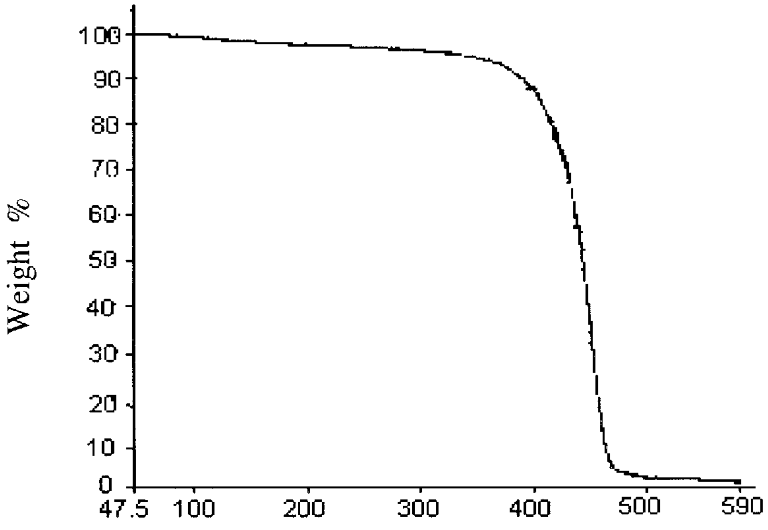
conversion. Extending the reaction time to 5 minutes gave quantitative conversions (run no.12). Polymerizations carried out at Al/Ni ratio 1000, and M/Ni ratio of 20,000 gave very high reaction rates. Under these conditions the catalyst activity was very high (run no. 15,16)

While most of the PNB were soluble in 1,2,4 trichlorobenzene at room temperature, some (run no. 13 and 14) gave turbid solutions. On heating above 100 °C all samples become clear. It was found that polynorbornene obtained by using MAO-I as cocatalyst had lower intrinsic viscosity as compared to poly(norbornene) obtained by using MAO-II. PNB obtained at higher M/Ni ratio had higher intrinsic viscosity. Again at high Al/Ni ratio polynorbornene with lower intrinsic viscosity were obtained.

The CP-MAS ^{13}C NMR spectrum of PNB (run no. 15) shows a sharp peak at 39.1 ppm (C_1 and C_3) and 30.6 ppm (C_5 and C_6) and few incompletely resolved peaks (Figure 1)

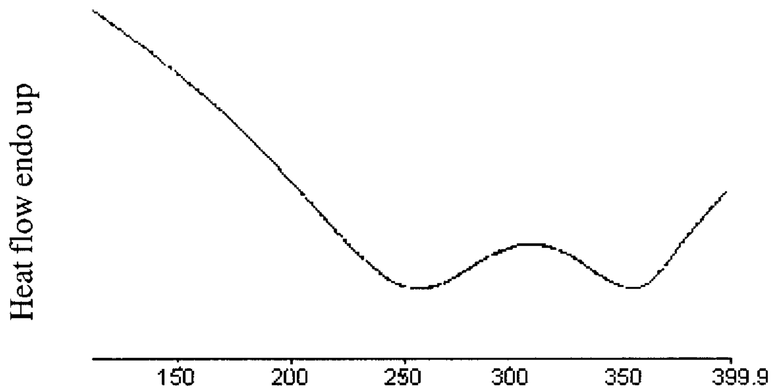
The IR spectra showed absence of double bond at 1620 cm^{-1} to 1680 cm^{-1}. Intense bands at 2946 cm^{-1} and 2896 cm^{-1} due to (C-H) stretching vibration and those at 1458 cm^{-1} and 1300 cm^{-1} due to (C-H) deformation were observed. The thermogravimetric analysis showed that the polymer was very stable upto 400 °C. The weight loss of 10 % was noted at 410 °C (Fig. 2).

The DSC analysis (Figure 3) showed a broad endotherm at 275 °C to 350 °C which is close to its decomposition temperature (Figure 2)



Temperature, °C

Figure 2.Thermogravemetric (TG) analysis of polynorbornene



Temperature °C

Figure 3. DSC curve of polynorbornene

Thus, Ni(II) salen in conjunction with MAO leads to soluble poly(norbornene)s via vinyl type polymerization of norbornenes. The catalyst activity is higher when MAO containing reduced free TMA is used as cocatalyst in a polar solvent such as chlorobenzene. High catalyst activity is observed at low catalyst concentration and high Al/Ni ratios.

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