

NMR SPECTROSCOPIC STUDY ON COPOLYMER OF ETHYLENE-NORBORNENE

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ABSTRACT

A series of ethylene-norbornene copolymers were synthesized using VO (OEt) Cl₂/Al₂Et₃Cl₃ catalytic system and their structure was characterized by ¹H-NMR, ¹H-¹H COSY NMR and ¹³C-NMR. Assignments of NMR spectra were given and discussed in detail.

INTRODUCTION

Copolymers of cyclic olefins are recognized for their interesting properties: non-crystallinity, optical transparency, low dielectric and high glass transition temperature^[1,2]. In the past, polymerization of cyclic olefins involving heterogeneous Ziegler-Natta catalytic systems only yield ring-opening products. Kaminsky present homopolymers of cyclic olefins, e.g. cyclopentene, norbornene and 1, 4, 5, 8-dimethano-1, 2, 3, 4, 4a, 5, 8, 8a-octahydronaphthalene(DMON) and their copolymers with ethylene or propylene using homogeneous Ziegler-Natta catalyst system based on combination of metallocene and methylaluminoxane (MAO)^[3-6]. These new materials were characterized by IR, NMR, DSC and X-ray diffraction methods.

The ¹³C-NMR investigations of the ethylene-cycloolefin copolymers indicate that incorporation and distribution of cyclic olefins in the copolymers greatly influence the properties of the materials, especially the glass transition temperature. A relationship between norbornene content in ethylene-norbornene copolymers and glass transition temperature was deduced by Kaminsky^[5]. A similar relationship in ethylene-DMON copolymers was also presented by Benedikt^[7]. But the detailed assignment of spectra remains uncertain.

A series of ethylene-norbornene copolymers containing different amount of norbornene were synthesized in the presence of VO(OEt) Cl₂/Al₂Et₃Cl₃ catalytic system. The structure of copolymers was characterized by NMR and fine assignment of the spectra is given in detail.

EXPERIMENTAL

All manipulations were performed under nitrogen atmosphere. ^1H -NMR and ^1H - ^1H COSY NMR spectra were recorded on Bruker AMX-400 at 120°C with $\text{C}_6\text{D}_4\text{Cl}_2$ as solvent. ^{13}C -NMR spectra were performed on JEOL FT-NMR 90 with HMDS as the internal standard at the same condition. DSC spectra were obtained on Perkin-Elmer DSC-7 at a heating rate of $20^\circ\text{C}/\text{min}$ and the result of the second scanning was recorded.

1. Materials

VOCl_3 , $\text{Al}_2\text{Et}_3\text{Cl}_3$ and norbornene (TCI) were obtained commercially. Ethanol was dried over MgSO_4 , *n*-hexane over 0.4 nm molecular sieve and norbornene with CaH_2 . Toluene serving as solvent was refluxed with sodium/benzophenone under inert atmosphere and distilled before use.

2. Preparation of $\text{VO}(\text{OEt})\text{Cl}_2$

To a 200 ml hexane solution of 0.1 mol VOCl_3 with magnetic stirrer, 0.1 mol ethanol in 50 ml hexane was added dropwise over 3 h at 0°C , while the evolved hydrogen chloride gas was absorbed by an aqueous NaOH solution. The resulting solution was stirred for another 2 h at room temperature. The solvent and unreacted reagents were evaporated at normal pressure. The mixture was finally distilled at $85^\circ\text{C}/2.5\text{ KPa}$ to give $\text{VO}(\text{OEt})\text{Cl}_2$ as bright yellow liquid (yield 64%).

3. Polymerization procedure

A typical polymerization is given here. To a 100 ml three-necked flask equipped with ethylene inlet and magnetic stirrer, 50 mmol norbornene and 0.5 mmol $\text{Al}_2\text{Et}_3\text{Cl}_3$ in 50 ml toluene were added. The mixture was stirred at 10°C and saturated with ethylene under normal pressure. Polymerization was initiated by injection of 0.025 mmol $\text{VO}(\text{OEt})\text{Cl}_2$ in toluene. After the reaction for 15 min, it was quenched with 50 ml ethanol. The copolymer was washed and finally dried at 60°C in vacuum to a constant weight.

RESULTS AND DISCUSSION

^1H -NMR and ^{13}C -NMR spectra of ethylene-norbornene copolymers prepared from $\text{VO}(\text{OEt})\text{Cl}_2/\text{Al}_2\text{Et}_3\text{Cl}_3$ catalytic system indicate that no ring-opening reaction occurs during polymerization. By varying norbornene/ethylene monomer ratio, a series of copolymers containing different amount of norbornene were synthesized and the activity is about $1.0\text{--}3.0 \times 10^5\text{ g copolymer/mol} \cdot \text{V} \cdot \text{h}$.

1. ^1H -NMR analysis of copolymer

Fig. 2 is the 400 MHz ^1H -NMR spectrum of ethylene-norbornene copolymer. The spectrum is complicate arising from the correlations between different types of protons. Combined with 400 MHz ^1H - ^1H COSY NMR spectrum of copolymer (Fig. 2), assignments are given in Table 1.

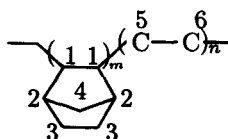


Fig.1 Structure of ethylene-norbornene copolymer

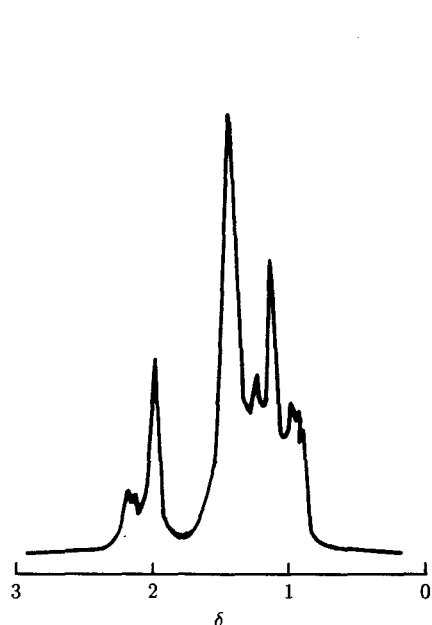


Fig. 2 400 MHz ^1H - NMR spec-
trum of ethylene-norbornene
copolymer

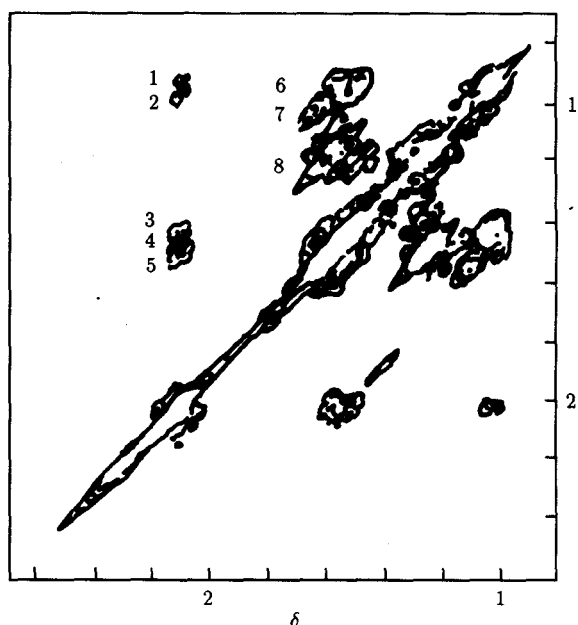


Fig. 3 400 MHz ^1H - ^1H COSY NMR spectrum of
ethylene-norbornene copolymer

Fig. 3 is the 400 MHz ^1H - ^1H COSY NMR spectrum of copolymer. It is shown that the proton on carbon 2 at 2.0 ppm correlate with five protons; one proton on carbon 1, two on carbon 3 and two on carbon 4; responsible for resonances 1 to 5. Because of the stereochemical configuration, each two protons on carbon 3, 4, 5 correlate with each other corresponding to the resonances 6, 7, 8. It is concluded that the main resonance at 1.42 ppm should be the contributions of protons on carbon 1, 3, 4 and 5. The resonance at 2.16 ppm, corresponding to the NN sequence, splits into two peaks. It may be considered that the monomer sequences of different

tacticities exist. The assignment of ^1H -NMR spectrum of copolymer is confirmed by the ^1H - ^{13}C HETCOR NMR spectrum of the same copolymer synthesized with $\text{Et}(\text{Ind})_2\text{ZrCl}_2\text{MAO}$ catalyst^[8].

2. ^{13}C -NMR analysis of copolymer

Fig. 4 shows the 90 MHz ^{13}C -NMR spectra of copolymers containing 3.8 mol% to 52.0 mol% norbornene. Kaminsky^[8] previously has made assignments for ethylene-norbornene copolymer ^{13}C -NMR spectra. Based on this prior work, assignments are given in Table 2 and the spectra can be resolved in more detail.

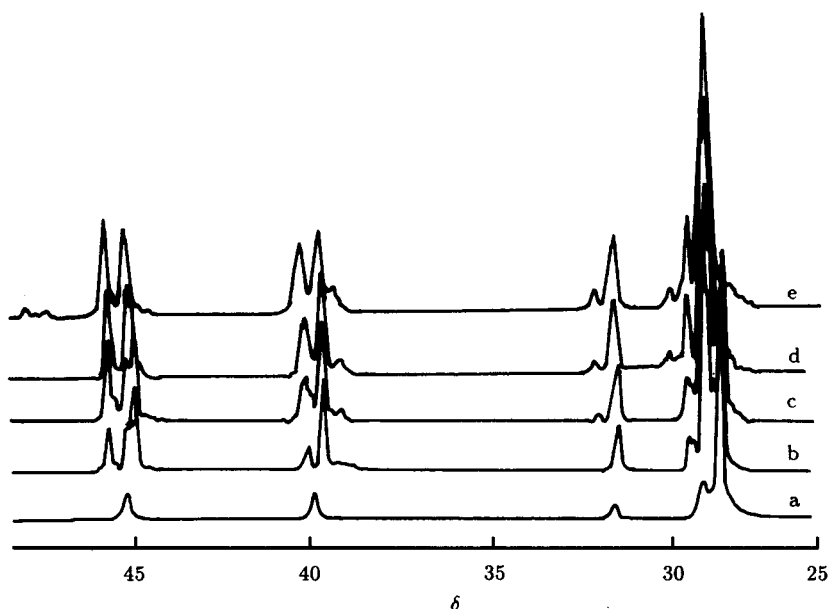


Fig. 4 90 MHz ^{13}C -NMR spectra of ethylene-norbornene copolymer containing (4a) 3.8; (4b) 24.6; (4c) 30.8; (4d) 40.5; (4e) 52.0 mol% norbornene

Fig. 4a shows ^{13}C -NMR spectrum of copolymer containing only 3.8 mol% norbornene. The spectrum is simple. The main resonance at 27.99 ppm is attributed to long block of ethylene in the polymer chain and the small signal at 28.47 ppm to the ethylene carbons in the NEE sequence. Two new resonances at 28.23 ppm and 28.52 ppm are observed in the spectra of copolymers containing high norbornene content, (Fig. 4b—4c) which correspond to ethylene in the EEE and NEN sequences. This presumption is demonstrated by the fact that the signal at 27.99 ppm and 28.23 ppm decrease while the resonance at 28.52 ppm becomes stronger as the content of norbornene increases; but only resonance at 28.52 ppm remains, corresponding to the NEN sequence, when the content of norbornene reaches 52.0 mol%. (Fig. 4e)

The ^{13}C -NMR signals of norbornene unit is more complicate than that of ethylene because both monomer sequence and stereochemical configuration must be

taken into account. The copolymers containing low norbornene content exhibit four resonances of norbornene unit and assignments are also given in Table 2. As the incorporation of comonomer increases, the two groups resonances related to carbon 1 and 2 become complicate and split, suggesting that different distribution of monomers and the tacticities of norbornene should be considered. In the spectra of copolymer with high norbornene content (Fig. 4e), two new signals at 47.45 ppm and 48.20 ppm are observed, suggesting that the material is a random copolymer of ethylene and norbornene with a certain portion of sequence being norbornene-norbornene.

Table 1 Assignments of ^1H -NMR spectrum of ethylene-norbornene copolymer

Chemical shift	Proton
0.88	H4
0.96	H3
1.10	H5
1.22	H1
1.42	H1, H3, H4, H5
1.96	H2 (ENE)
2.16	H2 (ENN)

Table 2 Assignments of ^{13}C -NMR spectra of ethylene-norbornene copolymer

Chemical shift	The carbons of ethylene	The carbons of norbornene
27.99	C5(—EE*E—)	
28.23	C5(EE*E)	
28.47	C5(NE*E)	
28.52	C5(NE*N)	
29.06		C3
31.20		C4
39.43		C2(NN*E)
39.84		C2(EN*E)
40.22		C2(NN*E)
45.39, 45.54		C1(EN*E)
46.08		C1(NN*E)
47.45		C1(NN*E)
48.20		C1(NN*E)

DSC investigation indicates that copolymer containing 24.6 mol% norbornene still has a melting point of 125°C while the copolymer having 14.0 mol% norbornene produced from metallocene/MAO catalyst is amorphous^[5]. It is evident that the copolymers obtained with different catalytic system have different monomer distributions. It is also the reason that even at low norbornene content, NN sequences exist in the polymer chain.

3. Mechanism

It was reported that the polycycloolefins are erythrodiisotactic when chiral metallocene catalysts are used^[4].

The ^{13}C -NMR spectra of ethylene-norbornene copolymers synthesized by metallocene show no splits because of their simple tacticity. But from spectra illustrated

above, splits is observed at high norbornene content. It can be deduced that a new norbornene monomer inserts randomly in view of configuration into the bond between the active center and the polymer chain terminated with norbornene unit because VO (OEt)Cl₂ involved in the polymerization is achiral catalyst. So different tacticities of NN sequence lead to the splits of resonance of carbon 1 and 2 and may be responsible for low glass transition temperature than the reported literature values.

CONCLUSION

Copolymer of ethylene-norbornene with different composition were synthesized in the presence of VO (OEt)Cl₂/Al₂Et₃Cl₃ catalytic system. Their structure were analyzed by ¹H, ¹³C, ¹H-¹H COSY NMR spectra and assignments were made in detail. The copolymers possess differential structure comparing with the copolymer obtained from metallocene because of the nature and the stereospecificity of the catalyst involved.

Keywords:

NMR spectroscopy; Ethylene/norbornene copolymer; Tacticity

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