

Copolymerization of ethylene with polar monomer by α - diimine nickel complex

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Abstract: Copolymerization of ethylene and ethyl acrylate was carried out by α -diimine nickel catalyst $[\text{ArN}=\text{CH}-\text{CH}=\text{NAr}]\text{NiBr}_2$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3(\text{CH}_3)_2$) in the presence of methylaluminoxane (MAO). The effects of experimental conditions in which mole ratio of Al/Ni, concentration of polar monomer, polymerization temperature, ethylene pressure and polymerization time varied on ethylene- ethyl acrylate copolymerization were investigated. The structures of the obtained copolymers were characterized by high-temperature NMR and FT-IR. It was found that Al/Ni mole ratio was 1000, the concentration of ethyl acrylate was 10 mmol/L, the polymerization temperature was 30 °C, the ethylene pressure was 10 atm, the polymerization time was 4 h, the molecular weight of the polymer and the incorporation of ethyl acrylate in the copolymer reached the good result.

1. Introduction

Olefin polymerization has achieved great success over the past 50 years. Of the many permutations available for modifying the properties of a polymer, the incorporation of functional groups into a nonpolar material is substantial.^[1-4] Polar groups exercise control over important properties such as toughness, adhesion, barrier properties, surface properties (paintability, printability), solvent resistance, miscibility with other polymers, and rheological properties. Specific targets, for example, include linear ethylene-vinyl acetate copolymers, random or linear copolymers of ethylene and acrylic acid,^[5] and propylene-vinyl alcohol copolymers possessing periodic hydroxyl groups that would fit within the polypropylene crystalline lattice without disruption. Not only would the important properties related to crystallinity be maintained (modulus, strength, solvent resistance), but new properties would also be expressed. An important feature of successful copolymerization of two monomers is the ability to control the amount and distribution of comonomer in the produced polymer. Aside from monomer concentration, the other important determinant in this process is the relative reactivity of the monomer pair.

In this paper, ethylene and ethyl acrylate was copolymerized by α -diimine nickel complex, $[\text{ArN}=\text{CH}-\text{CH}=\text{NAr}]\text{NiBr}_2$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3(\text{CH}_3)_2$) under activated by methylaluminoxane. The structures of the obtained copolymers were characterized by high-temperature NMR, high-temperature GPC, DSC and FTIR.

2. Materials

All air- and moisture-sensitive compounds were handled under an atmosphere of dried and purified argon using standard Schlenk techniques. Dichloromethane was distilled under an argon atmosphere



from CaH_2 prior to use. The complex $[\text{ArN}=\text{CH}-\text{CH}=\text{NAr}]\text{NiBr}_2$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3(\text{CH}_3)_2$) was synthesized according to the literature. ^[6] MAO (10 wt. % in toluene, containing ca. 30% AlMe_3) was purchased from ALBEMARLE CORPORATION and used as received. Ethylene monomer (99.9%) was supplied by Shanghai petrochemical company, and used after dehydration by 4\AA molecular sieve. Ethyl acrylate was supplied by China Pharmaceutical Group(AR).

3. Copolymerization of ethylene with ethyl acrylate (EEA)

In a clean and dry 150 mL stainless autoclave, a solution of the pre-catalyst and ethyl acrylate in solvent (50 mL) was introduced under ethylene atmosphere, and was saturated by ethylene. After the reaction temperature was established MAO was injected. The autoclave was sealed and rapidly pressurized to the desired ethylene pressure with fast stirring. The temperature was maintained by a water circulator. The consumed ethylene was measured by mass flow meter. After a desired reaction time, the reaction was quenched by venting the autoclave followed by addition of HCl /methanol (5% v). The precipitated polymers were filtered from solution and dried in vacuum.

4. Characterization

Nuclear magnetic resonance (NMR) analysis of the copolymer was performed on a Varian Unity 400 MHz spectrometer at $125\text{ }^\circ\text{C}$, using $\text{o-C}_6\text{D}_4\text{Cl}_2$ as solvent. ^1H NMR spectra were referenced to solvent peaks. The FT-IR were obtained by Nicolet MAGNA-IR 500 Fourier Transform Infrared Spectrometer.

5. Results and Discussion

The results of the copolymerization of ethylene and ethyl acrylate with Ni complex $[\text{ArN}=\text{CH}-\text{CH}=\text{NAr}]\text{NiBr}_2$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3(\text{CH}_3)_2$) are showed in Table 1. Comparing No.1, 2, 3, it is found that the catalytic activity reaches the highest (57.4 kg/molNi.h) when the Al/Ni mole ratio is 1000. It may be because the catalyst active center is fully activated at that condition. The Al/Ni mole ratio increases further, the catalytic activity decrease because of chain transfer caused by excess MAO. The concentration of polar monomer affects the catalytic activity and ethyl acrylate incorporation very much (No.2, 4, 5). The catalytic activity decreases with the concentration of polar monomer increasing, while ethyl acrylate incorporation increases with the concentration of polar monomer increasing. It may be because the high concentration of polar monomer will have a toxic effect on the catalytic activity center. Reaction temperature also affects the catalytic activity of the copolymerization very much as shown in Table 1, No.2, 6, 7. The suitable temperature is $30\text{ }^\circ\text{C}$. High temperature may shift the catalyst with low activity. The molecular weight decreases with temperature increasing, however, the incorporation of ethyl acrylate into the copolymer is affected little, around 4.2-4.3%. The effect of the polymerization time on the copolymerization is listed in Table 1, No.2, 8, 9. It shows that the catalytic activity reaches the highest (57.4 kg/molNi.h) when polymerization time is 4h. When the polymerization time is more than 4 h, the polymerization activity decrease, the molecular weight decreases too, however, the incorporation of ethyl acrylate into the copolymer increases to 4.6%. That means prolong the polymerization time is favor to the ethyl acrylate into the copolymer.

Table 1 Influence of reaction conditions on ethylene - ethyl acrylate copolymerization

| No. | Al/Ni mol/mol | EA (mmol/L) | T ($^\circ\text{C}$) | t (h) | Activity (kg/molNi.h) | $\text{M}_v \times 10^{-4}$ (g/mol) | EA Incorp. (mol%) |
|-----|------------------|----------------|---------------------------|----------|-------------------------------------|--|----------------------|
| 1 | 800 | 10 | 30 | 4 | 50.4 | 13.1 | 4.4 |
| 2 | 1000 | 10 | 30 | 4 | 57.4 | 11.2 | 4.6 |
| 3 | 1200 | 10 | 30 | 4 | 31.3 | 10.9 | 4.2 |
| 4 | 1000 | 5 | 30 | 4 | 81.6 | 13.6 | 1.3 |
| 5 | 1000 | 20 | 30 | 4 | 7.8 | 10.1 | 6.3 |

| | | | | | | | |
|---|------|----|----|---|------|------|-----|
| 6 | 1000 | 10 | 15 | 4 | 15.7 | 16.2 | 4.3 |
| 7 | 1000 | 10 | 40 | 4 | 13.7 | 2.3 | 4.9 |
| 8 | 1000 | 10 | 30 | 2 | 54.7 | 13.7 | 3.8 |
| 9 | 1000 | 10 | 30 | 8 | 29.3 | 4.0 | 4.6 |

Copolymerization conditions: catalyst: $[\text{ArN}=\text{CH}-\text{CH}=\text{NAr}]\text{NiBr}_2$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3(\text{CH}_3)_2$), 6.4 μmol , ethylene pressure: 10 atm, solvent: dichloromethane, $V_{\text{total}} = 50 \text{ mL}$.

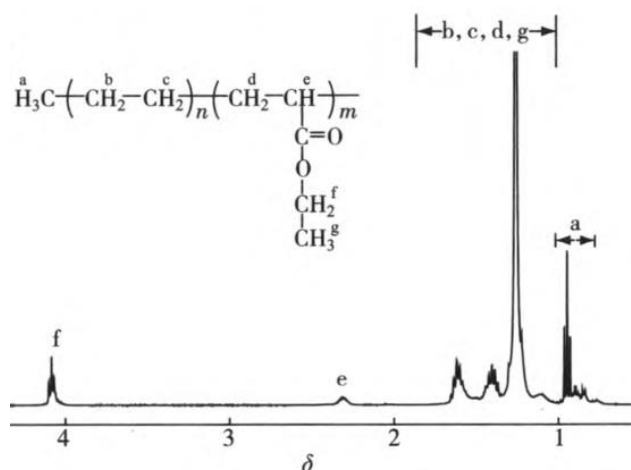


Figure 1 ^1H NMR spectrum of copolymer of ethylene with EA

The micro-structure of the copolymer of ethylene with ethyl acrylate is characterized by ^1H -NMR and FT-IR. The ^1H -NMR of the copolymer of ethylene with ethyl acrylate is illustrated in Figure 1. The peak at 4.09 ppm is the hydrogen atoms on the EA units (H_e), the peak at 2.30 ppm is the EA units (H_e). H_b , H_c , H_d and H_g on the methylene group is around 1.26 ppm, and the multiplet peaks around 0.9 ppm is the hydrogen on the methyl group at the terminal end of the ethylene chain.

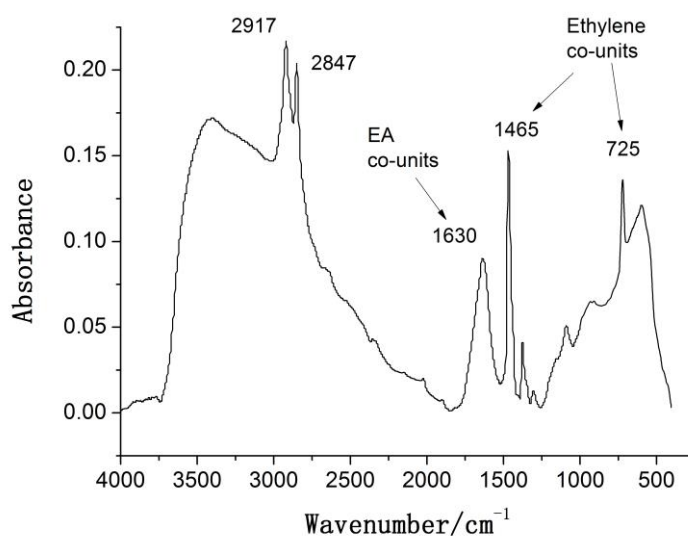


Figure 2 FT-IR of copolymer of ethylene with EA

The FT-IR of ethylene with ethyl acrylate copolymer is exhibited in Figure 2. 1630 cm^{-1} is the C = O stretching vibration peak on EA units, 1465 cm^{-1} is the CH bending vibration peak on EEA

methylene, 725 cm⁻¹ is the main chain of more than three methylene chain into a linear characteristic peaks.

From the ¹H NMR and FT-IR data, it can draw a conclusion that the obtained polymer is a copolymer of ethylene and ethyl acrylate.

6. Summary

Copolymerization of ethylene and ethyl acrylate was prepared by [ArN=CH-CH=NAr]NiBr₂ (Ar = 2,6-C₆H₃(CH₃)₂) in the presence of methylaluminoxane (MAO). The effects of polymerization conditions, such as mole ratio of Al / Ni, concentration of polar monomer, polymerization temperature, ethylene pressure and polymerization time were investigated. It results show that when Al /Ni mole ratio was 1000, the concentration of ethyl acrylate was 10 mmol/L, the polymerization temperature was 30 °C, the ethylene pressure was 10 atm, the polymerization time was 4 h, the molecular weight of the polymer and the insertion rate in the copolymer reached the best results. Above all, from the characterization of the polymer we can draw a conclusion that the polymer we obtained is the copolymer of ethylene with ethyl acrylate.

References

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