

Note

POLYKETONE FROM ETHYLENE WITH CARBON MONOXIDE CATALYZED BY NOVEL CATALYST SYSTEMS BASED ON COPPER WITH BIDENTATE PHOSPHORUS CHELATING LIGANDS

Jun Huang, Feng-bo Li, Jin Zou and Guo-qing Yuan*

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Xiu-li Shi and Ding-sheng Yu

College of Material Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

Abstract Copolymerization of ethylene with carbon monoxide was performed with Cu catalyst systems. Novel catalyst systems based on Cu ($\text{Cu}(\text{CH}_3\text{COO})_2$ /ligand/acid) were firstly reported for the copolymerization of ethylene with carbon monoxide, in which the ligand was a bidentate phosphorus chelating ligand. The experimental results showed that this kind of Cu catalyst system exhibited high activity. When DPPP (1,3-bis(diphenylphosphine)propane) and CH_3COOH were used as ligand and acid, the corresponding catalyst system had the best activity of 108.1 g copolymer/(gCu · h). The novel Cu catalyst system had the advantages of high stability and low cost.

Keyword Copper catalyst, Copolymerization, Ethylene, Carbon monoxide, Polyketone

INTRODUCTION

Copolymerization of ethylene with carbon monoxide has attracted great interest recently in both academia and industry. A great advance in the application of Pd(II) catalyst systems for the production of perfectly alternating copolymer from carbon monoxide and ethylene occurred when Drent and coworkers discovered that the bidentate ligand (DPPP) used as a ligand to complex with the Pd(II) atom through dative bonds, together with the presence of a strong acid, resulted in a considerable rate enhancement^[1, 2]. But problems still existed, *e.g.* Pd is expensive and difficult to recover in the industrial process.

Some other metals were found to be active for copolymerization of ethylene and carbon monoxide, especially nickel complexes^[3, 4]. Can copper be used to replace the relatively expensive palladium as the central metal of the catalyst? In this study, a novel catalyst based on Cu(II) is first reported for the copolymerization of ethylene with carbon monoxide. The product polyketone was characterized by ^1H -NMR and ^{13}C -NMR, and confirmed definitively as a perfectly alternating copolymerized product.

Copolymerization was carried out in a 100 mL stainless steel autoclave. First, solid catalyst compounds including $\text{Cu}(\text{CH}_3\text{COO})_2$ and ligand were weighed accurately and added to the autoclave directly, the solvent containing strong acid was introduced, then the autoclave was sealed and purged with ethylene at least three times, and ethylene was charged to experimental pressure. After equimolar CO was introduced at about 6.0 MPa the autoclave was heated to the chosen temperature. After reaction for 1–12 h, the autoclave was rapidly cooled, and the unreacted gases were vented. The product slurry was filtered off, washed with methanol, and dried in air to give a snow-white powder. The average catalytic activity was calculated from copolymer weight as unit of g copolymer/(gCu · h).

*Corresponding author: Guo-qing Yuan (袁国卿), E-mail: yuangq@infoc3.icas.ac.cn

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$\text{Cu}(\text{CH}_3\text{COO})_2/\text{ligand}/\text{acid}$ catalyst systems were studied with different strong acids under conditions of 90 °C and 6.0 MPa. The results are listed in Table 1.

Table 1. Copolymerization of ethylene with CO: effect of acid

$\text{Cu}(\text{CH}_3\text{COO})_2$ (mmol)	DPPP (mmol)	Acid (2 mL)	Activities g copolymer/(gCu · h)
0.10	0.15	CF_3COOH	108.4
0.10	0.15	$\text{CH}_3\text{SO}_3\text{H}$	86.9
0.10	0.15	HBF_4	78.2
0.10	0.15	0	0
0.10 ^a	0.15	0	0

Reactive condition: 90 °C and 6.0 MPa, DPPP = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$

^a $\text{Cu}(\text{CF}_3\text{COO})_2$, Reaction time: 3 h

Table 1 shows clearly that without acid, $\text{Cu}(\text{CH}_3\text{COO})_2/\text{DPPP}$ catalyst system had very weak activity and no product was obtained. When strong acid was introduced, the $\text{Cu}(\text{CH}_3\text{COO})_2/\text{DPPP}/\text{acid}$ catalyst system exhibited high activity. When CF_3COOH , $\text{CH}_3\text{SO}_3\text{H}$ and HBF_4 were used as acid, the activities of the corresponding catalyst systems were 108.4, 86.9 and 78.2 g copolymer/(gCu · h) respectively.

$\text{Cu}(\text{CH}_3\text{COO})_2/\text{ligand}/\text{CF}_3\text{COOH}$ catalyst systems were studied with 3 different ligands under conditions of 90 °C and 6.0 MPa. The activities and stabilities of the three catalyst systems with DPPP, DPPE (1,2-bis(diphenylphosphine)ethane) and DPPB (1,4-bis(diphenylphosphine)butane) were studied, and the results were as in Fig. 1.

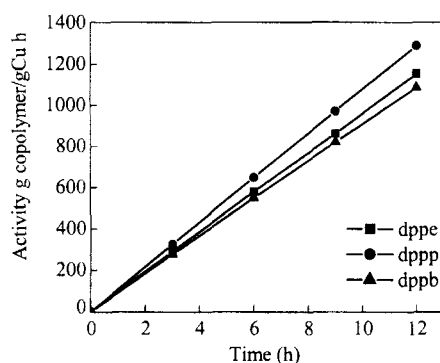


Fig. 1 Copolymerization of ethylene and CO: effect of ligand in catalytic activity and stability

DPPP = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$; DPPE = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$;

DPPB = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$

Figure 1 shows clearly that the DPPP was the best among the three ligands, and the catalyst systems were very stable for the copolymerization of ethylene with carbon monoxide. The main reason was suggested that the six-coordinated Cu cation complex could be formed with DPPP, which was relatively stable as the catalyst active species. With DPPE and DPPB, five- and seven-coordinated Cu cations were formed respectively, which were not as stable as the six-coordinated complex. The copolymerization rates were maintained at 107, 96, and 89 g copolymer/(gCu · h) for DPPP, DPPE and DPPB respectively, and no evident deactivation was observed for these catalyst systems in 12 h.

In order to prove that the product from the new Cu based catalyst systems was linear alternating polyketone, here the ^1H -NMR, ^{13}C -NMR spectra of polyketone prepared with $\text{Cu}(\text{CH}_3\text{COO})_2/\text{DPPP}/\text{CF}_3\text{COOH}$ catalyst system were recorded.

The ^1H -NMR, ^{13}C -NMR spectra are shown in Figs. 2, 3, and the assignments are listed in Table 2. Except for the spectra of solvent (CF_3COOD), the spectra were very simple. The spectra were in agreement with

perfectly alternating polyketone structure.

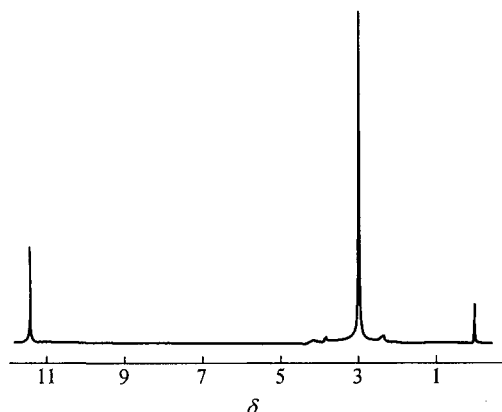


Fig. 2 ^1H -NMR spectrum of polyketone from $\text{Cu}(\text{CH}_3\text{COO})_2/\text{DPPP}/\text{CF}_3\text{COOH}$

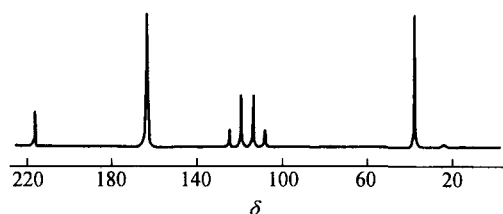


Fig. 3 ^{13}C -NMR spectrum of polyketone from $\text{Cu}(\text{CH}_3\text{COO})_2/\text{DPPP}/\text{CF}_3\text{COOH}$

Table 2. Attributions of the ^1H -NMR and ^{13}C -NMR spectra

^1H -NMR (δ)			^{13}C -NMR (δ)		
11.45	2.89	217.3	163.1	118.3	38.9
$\text{CF}_3\text{COO}^*\text{H}$	$\text{C}^*\text{H}_2\text{CH}_2\text{CO}$	$^*\text{CO}$	CF_3^*COOH	$^*\text{CF}_3\text{COOH}$	$^*\text{CH}_2\text{CH}_2\text{CO}$

Solvent: CF_3COOD

Compared with Pd based catalyst systems^[5], Cu based catalyst systems are inexpensive and very stable. Although the activity of Cu catalyst systems is not as high as that of Pd catalyst systems^[6], a Cu catalyst system has been reported, and perhaps another optimized Cu catalyst system could be very active and replace the palladium in manufacture.

REFERENCES

- 1 Drent, E. and Budzelaar, P.H.M., *Chem. Rev.*, 1996, 663
- 2 Sommazzi, A. and Garbassi, F., *Prog. Polym. Sci.*, 1997, 22: 1547
- 3 Domhover, B., Klau, W., Kremer, A., Bell, A.R. and Mootz, D., *Angew. Chem. Int. Ed.*, 1998, 37: 21
- 4 Klau, W., Bongards, J. and Reib, G.J., *Angew. Chem. Int. Ed.*, 2000, 39 (12): 3894
- 5 Gambs, C., Chaloupka, S., Chaloupka, S., Consiglio, G. and Togni, A., *Angew. Chem. Int. Ed.*, 2000, 39: 2486
- 6 Milani, B. and Mestroni, G., *Comment on Inorganic Chemistry*, 1999, 20 (4–6): 301