

Terpolymerization of Carbon Monoxide, Styrene, and 4-Methylstyrene Catalyzed by Palladium-Rare Earth Catalyst

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Received February 14, 2008; Revised December 15, 2008; Accepted December 31, 2008

Abstract: In order to improve the thermomechanical performance of polyketone, a third monomer (4-methylstyrene) was added to the copolymerization system. The terpolymer of CO, styrene, and 4-methylstyrene was synthesized in the presence of multicomponent catalysts containing palladium acetate and rare earth metal phosphonates. The products were characterized by infrared spectroscopy (IR), and nuclear magnetic resonance spectroscopy (NMR). The effects of the different components, including the third monomer, palladium acetate, 2,2'-bipyridyl, rare earth phosphonate, *p*-toluene-sulphonic acid, and *p*-benzoquinone, were also studied. The highest catalytic activity of 965.51 g/(gPd·h) was obtained with a catalyst containing palladium acetate and rare earth phosphonate.

Keywords: polyketone, rare earth phosphonate, styrene, carbon monoxide, terpolymerization, catalytic activity.

Introduction

The polyketone can be prepared by the copolymerization of carbon monoxide and alkene.¹ Properties of the copolymer vary with different alkenes and copolymerization methods. The earlier researches mainly focused on the copolymerization of CO and ethene, which was initiated by free radical and irregular polyketone was obtained.² Until recent decades, the copolymer with strictly alternative structure synthesised by CO and styrene obtained by the transition metal catalyst have been mainly discussed.^{3,4} However, like many others polymer with the highly stereospecific structure,⁵ it results the high melting temperature and brings huge trouble to the product processing. Furthermore, with the noble metal palladium as a main catalyst, the high cost also impedes the industrialization of polyketone synthesis.

With the development in the study of the rare-earth catalyst, the rare-earth exhibits excellent assistant catalytic effect in many systems. Special attention has been paid to the results such as hydrogenation of CO, CO₂,⁶ synthesis of amine,⁷ and copolymerization of conjugated diene.⁸

Here, the palladium acetate as a main catalyst and rare earth salts as the cocatalysts were used in this system to reduce the amount of palladium. Furthermore, the third monomer, 4-methylstyrene was also introduced to the system to modify the chain structure of the product, to lower its melting point, and to improve its machinability. The effects of every component in the complex catalytic system on the

catalytic activity and properties of the product were investigated.

Experimental

Raw Materials. Palladium acetate (AR, ACROS Organics, NJ, USA); carbon monoxide (Hepubei Air Industry Ltd., Beijing, China); *p*-toluene-sulphonic acid (AR, Huazhen Special Chemicals Factory, Tianjin, China); rare earth oxide (>99.9%, Rare Earth Research Institute, Baotou, China); 4-methylstyrene (AR, Aldrich); The other chemicals were of analytical grade or higher (Kewei Ltd., Tianjin, China), and thus they were directly used without further purification.

Preparation of Rare Earth Salts. According to the method mentioned in reference,⁹ rare earth phosphonate was prepared using rare earth oxide (Nd₂O₃, Pr₂O₃, Eu₂O₃, Ho₂O₃) and P₂₀₄. To a solution of 15 mL concentrated hydrochloride acid was added 10 g of rare earth oxide. The mixture was heated until the precipitation occurred, and then a mixed solvent of water and alcohol (1:1 wt%) was added. 60 g of P₂₀₄ was also added slowly to the rapidly stirred mixture and the resulting solution was at room temperature for several hours. The pH was adjusted to 6.5 by dilute ammonia solution. The white precipitation was filtrated, washed by ethanol, and dried in vacuum for future use.

Copolymerization. The catalytic system used in this paper was composed of palladium acetate, and ruthenium phosphonate (praseodymium phosphonate, europium phosphonate, holmium phosphonate). A mixture of methanol (6 mL), styrene (10 mL), 4-methylstyrene (5 mL), *p*-toluene-sulphonic

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acid (1.5×10^{-4} mol), palladium acetate (0.2×10^{-4} mol), 2,2'-bipyridine (1.5×10^{-4} mol), and the oxide, *p*-benzoquinone (20×10^{-4} mol), were placed in a 100 mL electromagnetic stirring stainless steel autoclave. The reactor was then pressurized to 2 MPa with CO. The reactor was kept in a 60 °C water bath and under constant pressure of 2 MPa for 2 h after checking the sealing. The autoclave was cooled down to room temperature after the copolymerization, and the unreacted CO was released. Ethanol was used to wash the precipitation. The white powder was obtained after washing, filtration, and drying.

Calculation of Catalytic Activity (*R*). The catalytic activity *R* can be calculated by the equation below:

$$R = \frac{\text{Polyketone(g)}}{\text{Pd(g)} \times \text{Time(h)}}$$

where *R* is the catalytic activity (gPK/(gPd·h)).

Measurements. The structure of copolymer was investigated by the Bio-Rad FTS 3000 spectrometer. Solid-state ^{13}C NMR spectra were acquired on Varian Infinity plus 300WB NMR spectrometer operating at 75 MHz. The melting point of the copolymer was measured by a RY-2 melting point apparatus (Tianjin Analysis Instrument CO., LTD., P.R. China). Molecular weights and molecular weight distributions were measured with a Waters 1515 gel permeation chromatograph (GPC) equipped with a Waters 2410 differential refractometer as detector. Three Styragel columns (HR2, HR4, HR6) were used in series. GPC samples were run at 40 °C with THF as the mobile phase at a flow rate of 1 mL/min, and the columns were calibrated using narrow distribution polystyrene standards obtained from Polymer Laboratories Ltd. UK.

Results and Discussion

Characterization. The IR spectrum of the terpolymer is shown in Figure 1. It is shown that the product have a strong characteristic absorption peak of ketone at 1705.9 cm^{-1} . Besides, absorption peaks at 698.4 cm^{-1} and 751.9 cm^{-1} are induced by the out-of-plane bending vibration of =CH on the benzene. It is the benzene single substitution characteristic absorption band. There are also several absorption peaks from 1453.6 to 1603.0 cm^{-1} , which are caused by the vibration of the benzene skeleton. These absorption peaks confirm the terpolymerization of CO/ST or 4-MeST.

The ^{13}C solid-state NMR spectrum of the copolymer was shown in Figure 2. The resonances at 44.3, 54.2, and 208.5 ppm in the ^{13}C NMR spectrum were assigned to backbone methine, methylene, and carbonyl carbons, respectively, of the molecular unit $-\text{CH}_2\text{CHphCO}-$. The aromatic carbon resonances were located at 128.6, 133.3 and 137.8 ppm, whilst the resonance at 21.6 ppm represented the methyl of 4-methylstyrene. Thus, the chemical shifts corresponding to the C atoms in various chemical environments confirmed

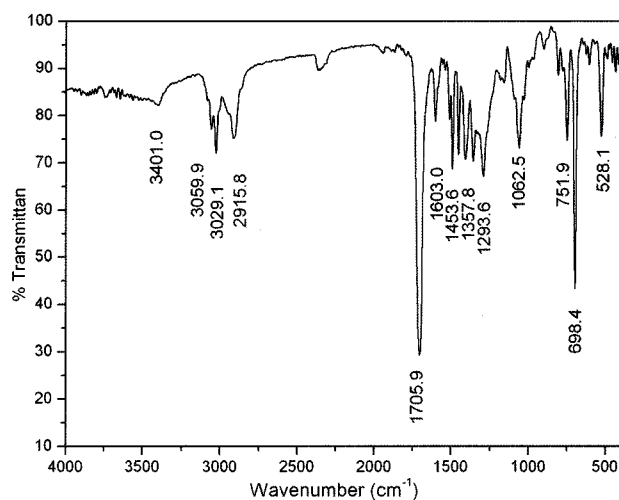


Figure 1. FTIR spectrum of terpolymerization of CO/ST or 4-methylstyrene.

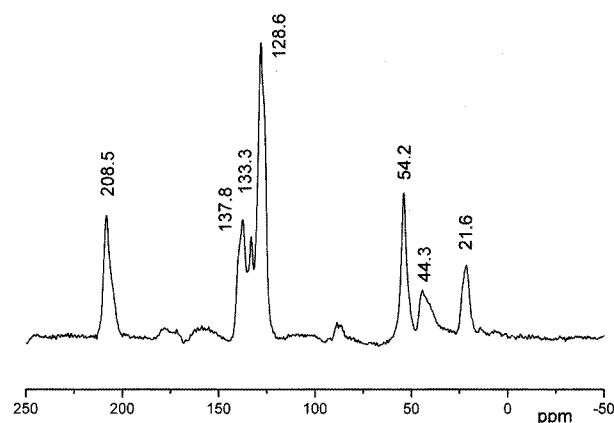


Figure 2. NMR spectrum of terpolymerization of CO/ST or 4-methylstyrene.

the structure of tri-copolymer of CO/ST/4-methylstyrene.

Effects of Different Rare Earth Materials on Copolymerization. Effects of different rare earth materials on the catalytic activity were compared, and the results are listed in Table I. From Table I, one can generalise that rare earth can increase yield of the polymer efficiently. The mechanism of the reaction is probably that Scheme I may be transformed into Scheme II. In this way, probably more than 2 times of the active centres could be kept in the catalytic system and so the catalytic activities were improved in the initiation steps of the copolymerization. Among them, holmium has the higher catalytic activity of 965.51 gPK/(gPd·h). From praseodymium salt to holmium salt, the catalytic activity of the system increases with number of orbital electrons. However, the catalytic activity of system in the presence of pure rare earth salt is zero under similar conditions (Table I, entry 6). The effect of different rare earth elements on the molecular weight in the catalytic system was also presented in

Table I. Effect of Different Rare Earth Phosphonate on the Catalytic Activity

Entry ^a	Rare Earth Salts	Electron Configuration	Color	M_w^b	PDI ^c	R (gPK/(gPd·h))
1	Pd ²⁺ +Pr ³⁺	4f ⁵ 6s ²	white	12,909	1.56	695.36
2	Pd ²⁺ +Nd ³⁺	4f ⁶ 6s ²	white	17,965	1.64	815.17
3	Pd ²⁺ +Eu ³⁺	4f ⁷ 6s ²	white	20,270	1.66	942.02
4	Pd ²⁺ +Ho ³⁺	4f ¹¹ 6s ²	white	21,509	1.82	965.51
5	Pd ²⁺	-	white	24,239	1.82	420.66
6	Ho ³⁺	4f ¹¹ 6s ²	-	-	-	0

^aReaction conditions: palladium acetate 0.2×10^{-4} mol, rare earth phosphonate 0.4×10^{-4} mol, methanol 6 mL, 2,2'-bipyridine 1.5×10^{-4} mol, *p*-benzoquinone 20×10^{-4} mol, *p*-toluene-sulphonic acid 1.5×10^{-4} mol, duration 2 h, temperature 60 °C, pressure 2 MPa. ^b M_w is the weight average molecular weight. ^cPDI is polydispersity index (M_w/M_n).

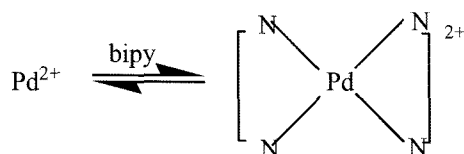
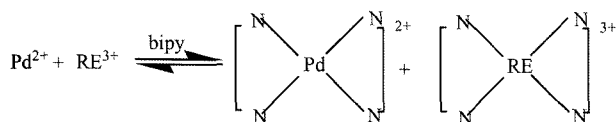

Scheme I. Schematic representation for the role of Pd²⁺ in the catalytic system.

Scheme II. Schematic representation for the role of RE³⁺ in the catalytic system.

Table I. A change of the rare earth salt from praseodymium-acetate to holmium acetate resulted in an increase of the molecular weight (from 12,909 in the presence of praseodymium phosphonate to 21,509 in the presence of holmium phosphonate). It is an unexpected finding that the rare earth complex catalytic systems (Table I, entry 1-4) maybe result in a lower molecular weight products compared to Pd²⁺ catalytic system (Table I, entry 5) under similar conditions, although the

Table II. Effect of Monomer Ratio on Catalytic Activity and Thermodynamics Performance

Entry ^a	Ratio ^b	T_m (°C)
1	10:0	256
2	10:1	255
3	8:1	245
4	6:1	241
5	4:1	236
6	2:1	230

^aReaction conditions: palladium acetate 0.2×10^{-4} mol, neodymium phosphonate 0.4×10^{-4} mol, methanol 6 mL, 2,2'-bipyridine 1.5×10^{-4} mol, *p*-benzoquinone 20×10^{-4} mol, *p*-toluene-sulphonic acid 1.5×10^{-4} mol, duration 2 h, temperature 60 °C, pressure 2 MPa. ^bVolume ratio of styrene to 4-methylstyrene.

complex catalytic system exhibited high activity.

Effect of Monomer Ratio on the Catalytic System. The volume ratio of styrene to 4-methylstyrene is also observed to affect the catalytic activity. Results are shown in Table II and Table III, entries 1-6. The catalytic activity irregularly changes with different ratios of styrene/4-methylstyrene. On the other hand, the melting point of products depends on this ratio. Since the introduction of 4-methylstyrene would cause the change of packing of the strict linear alternative structure, the melting points decrease with the increase of this ratio as expected.

Effect of Rare Earth Amount on Catalytic Activity. In this experiment, rare earth phosphonate is introduced to the system as a co-catalyst. Effect of the rare earth amount on the catalytic activity was obtained from Table III, entries 7-11. When the palladium acetate amount is 0.3×10^{-4} mol, the increase in the neodymium phosphonate amount causes a dramatic increase in the catalytic activity. The best catalytic effect is obtained when the Nd to Pd ratio is 2:1, and the catalytic activity is 815.17 gPK/(gPd·h). The catalytic activity decreases when the amount of the neodymium further increase. In this copolymerization system, the bidentate ligand and palladium can easily form a chelate structure. When the chelate single ring structure is formed, suitable activities vacancy is provided and the system shows higher catalytic activity. However, when excess amount of Nd is used, 2,2'-bipyridine is consumed partly. The active centre of Pd²⁺ becomes unstable and further loses its catalytic activity.

Effect of 2,2'-Bipyridine Amount on Catalytic Activity. Ligands that contain phosphorous or nitrogen is usually selected to chelate with metal catalyst to improve the stability of the catalyst. The bidentate ligand has better effect than monodentate ligand¹⁰ in the copolymerization. In this paper, 2,2'-bipyridine is selected as the ligand for palladium catalytic system. Table III entries 12-17, shows significant effect of the 2,2'-bipyridine/Pd²⁺ molar ratio on the catalytic activity. The catalytic activity of the copolymerization system first increases as the amount of 2,2'-bipyridine increase. It reaches the maximum, 815.2 gPK/(gPd·h), when the molar

Table III. Effects of Different Components on the Catalytic Activity^a

Entry	R ^b	4-MeST ^c	Bipy ^d	Nd ^e	BQ ^f	pTSA ^g
1	516.8	0	1.5	0.4	20	1.5
2	512.1	1	1.5	0.4	20	1.5
3	803.4	1.25	1.5	0.4	20	1.5
4	636.6	1.7	1.5	0.4	20	1.5
5	528.6	2.5	1.5	0.4	20	1.5
6	815.2	5	1.5	0.4	20	1.5
7	458.1	5	1.5	0.2	20	1.5
8	697.7	5	1.5	0.3	20	1.5
9	815.2	5	1.5	0.4	20	1.5
10	740.0	5	1.5	0.5	20	1.5
11	404.1	5	1.5	0.6	20	1.5
12	655.4	5	1.2	0.4	20	1.5
13	747.0	5	1.4	0.4	20	1.5
14	815.2	5	1.5	0.4	20	1.5
15	772.9	5	1.6	0.4	20	1.5
16	723.6	5	1.8	0.4	20	1.5
17	690.7	5	2.0	0.4	20	1.5
18	493.3	5	1.5	0.4	20	1.2
19	587.3	5	1.5	0.4	20	1.4
20	815.2	5	1.5	0.4	20	1.5
21	714.2	5	1.5	0.4	20	1.6
22	653.1	5	1.5	0.4	20	1.8
23	527.4	5	1.5	0.4	10	1.5
24	815.2	5	1.5	0.4	20	1.5
25	637.7	5	1.5	0.4	30	1.5
26	563.8	5	1.5	0.4	40	1.5

^aReaction conditions: palladium acetate 0.2×10^{-4} mol, styrene 10 mL, methanol 6 mL, reaction time=2 h, temperature=60 °C, $P_{CO}=2$ MPa. ^bR defined as g polyketone/(gPd·h). ^cDosage of 4-methylstyrene. ^dDosage of 2,2'-bipyridine ($\times 10^{-4}$ mol). ^eDosage of neodymium phosphonate ($\times 10^{-4}$ mol). ^fDosage of *p*-benzoquinone ($\times 10^{-4}$ mol). ^gDosage of *p*-toluenesulphonic acid ($\times 10^{-4}$ mol).

ratio of 2,2'-bipyridine to Pd²⁺ is 7.5. The catalytic activity decreases when the molar ratio is higher than 8.0.

Effect of *p*-Toluene-sulphonic Acid Amount on Catalytic Activity. The important roles of the *p*-toluene-sulphonic acid are found in the catalytic system.^{11,12} (1) It can replace the acetate ion, which has strong chelating ability with Pd²⁺, so that the reacting monomers can easily be activated by coordination to the central metal ion. (2) It can increase the concentration of active Pd-hydride species by the reactivation of Pd(0) complexes. In Table III, entries 18-22, when the

molar ratio of *p*-toluene-sulphonic acid to Pd²⁺ increases, the catalytic activity increases dramatically. It reaches the maximum of 815.2 gPK/(gPd·h) with the molar ratio of 7.5. However, further increase of the molar ratio decreases the catalytic activity. The results is probably that when the molar ratio of *p*-toluene-sulphonic acid/Pd²⁺ is much higher (>7.5), it may react with 2,2'-bipyridyl. A decrease in the catalytic activity of the system may be due to the amount loss of 2,2'-bipyridyl.

Effect of *p*-Benzoquinone Amount on Catalytic Activity.

In the terpolymerization of CO, styrene, and 4-methylstyrene, *p*-benzoquinone (BQ) addition has the following affects:^{13,14} first of all, it chelates with Pd⁰ and helps Pd⁰ re-enter the catalytic system by ion exchanging with solvent; secondly, it is also used as a strong oxidizer, which prevents the transition of the Pd²⁺ to Pd⁰. Hence, optimal amount of the *p*-benzoquinone improves the reaction catalytic activity.

Table III, entries 23-26 shows that the maximum catalytic activity, 815.2 gPK/(gPd·h), is obtained when the molar ratio of BQ to Pd is 100. As the amount of BQ further increases, the catalytic activity of the system decreases. It is also observed in this experiment that with the increasing amount of BQ, the colour of polyketone changes from grey to red. The grey color of the polyketone is due to the existence of Pd metal. The white colour shows that there is no Pd metal contained in the product. When the ratio of BQ/Pd²⁺ is 200, the product shows red in colour. This is due to the excess amount of BQ is applied, which makes the system non-homogeneous and affects the catalytic activity.

Conclusions

Tri-copolymer was synthesized by using CO, ST, and 4-methyl ST under in present of Pd²⁺-rare earth multiplex catalyst system. Effects of each composition of the catalytic system on the catalytic activity were explored. The effect of different monomer ratio on properties of products was also obtained. An increase in the amount of third monomer, 4-methylstyrene, resulted in the remarkable decrease in the melting point of the copolymers. The results presented may be applied to find more suitable third monomer and catalyst system in copolymerization of CO with styrene.

Acknowledgements. The authors are grateful for the financial support of this work by the National of Nature Foundation of China (No. 20476080) and Tianjin Natural Science Foundation (No. 07JCYBJC00600).

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