Research Article

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Copolymerization of CO$_2$, propylene oxide, and itaconic anhydride with double metal cyanide complex catalyst to form crosslinked polypropylene carbonate

https://doi.org/10.1515/epoly-2021-0082
received July 20, 2021; accepted September 20, 2021

Abstract: In this study, a high-activity Zn–Co double metal cyanide complex was synthesized and used to catalyze the ternary polymerization of carbon dioxide, propylene oxide, and itaconic anhydride to produce a new class of polypropylene carbonates characterized by excellent performance and low ether content. The number average molecular weight of the terpolymer was as high as 2.14 × 10$^5$ g·mol$^{-1}$, and the polydispersity index was as high as 1.58. In the case of PPCIAn$_3$, the 5% weight loss temperature increased by 70°C, the total weight loss temperature increased by 100°C, the tensile strength increased by 6.6 MPa, and the elongation at break decreased to 14.5% with respect to traditional polypropylene carbonate. The apparent efficiency of the catalyst was as high as 45.79 kgpolymer/kgcatalyst, indicating its high catalytic activity. $^1$H-NMR spectrometry, gel permeation chromatography, differential scanning calorimetry, thermogravimetric analysis, and in situ Fourier-transform infrared spectroscopy were used to characterize the polymerization process and the structural properties of the obtained terpolymers.

Keywords: ternary copolymerization, carbon dioxide, double metal cyanide complex, terpolymerization, green chemistry

1 Introduction

Carbon dioxide (CO$_2$) is an ideal C1 raw material because it is abundant, cheap, nontoxic, and nonflammable; moreover, it is an inexhaustible resource (1). Controlling CO$_2$ emissions and making effective use of this compound have become a strategic research topic for various countries. In fact, given that CO$_2$ is a major greenhouse gas, converting it into products with commercial value is becoming an increasingly important objective (2–4). The synthesis of biodegradable polycarbonates relying on CO$_2$ as a raw material has become the focus of current CO$_2$ research. This transformation does not just fix the abundant CO$_2$ resources present in the atmosphere and, to a certain extent, alleviate the greenhouse effect associated with the excessive CO$_2$ emissions, but it also realizes the recycling of resources. It can also be used as a way to provide new chemical resources that can be used to alleviate the shortage of chemical raw materials. Therefore, whether viewing it from the perspective of environmental protection or resource utilization, the chemical conversion of CO$_2$ to useful chemicals is highly significant, and it has broad application prospects (5), and it conforms to the major national strategic needs of “energy saving and emission reduction” and the concept of “green and sustainable development.”

CO$_2$ is quite stable thermodynamically, with a bond angle of 180°. Therefore, the use of CO$_2$ as a reactant in chemical reactions is a huge challenge in contemporary chemistry. Among them, CO$_2$ and epoxides (such as propylene oxide [PO], ethylene oxide, cyclohexene oxide, and styrene oxide) are alternately copolymerized to prepare biodegradable polycarbonate, which is considered...
to be one of the most potential green polymerization processes (Scheme 1). In addition, due to the environmentally friendly properties of polycarbonate, such as atomic economy, energy saving, and biodegradability, as well as its application in the building materials industry, automobile manufacturing, aerospace, biomedicine, medicine, and other fields, it has become an important research topic (6). However, in practical applications, the glass transition temperature of the copolymer obtained from CO2 and alkylene oxide is very low, the strength is low at high temperature, its brittleness is a serious issue at low temperature (7), its mechanical properties are not ideal, the molecular chain contains relatively soft ester bonds and a small amount of polyether segments, the flexibility of the molecular chain becomes larger and the interaction force becomes smaller, and its thermodynamic and mechanical properties need to be improved (8,9). In this context, ternary copolymerization is an effective approach to improve the performance of polypropylene carbonate (PPC).

Since the 1969 publication of the milestone study in which Inoue et al. (10) used ZnEt2/H2O to synthesize polycarbonate, many studies have focused on finding CO2/epoxy compounds alternating copolymerization catalysts with higher activity and selectivity. Indeed, catalytic systems have been developed that have been observed to improve reaction efficiency (11–19).

Double metal cyanide (DMC) is a well-known, excellent catalyst for epoxy ring-opening polymerization and the copolymerization of epoxide and CO2 (20–24). DMC is characterized by high stability, high reactivity, and moisture resistance, so it is a very attractive heterogeneous system (25).

Itaconic anhydride (IAn) is an important itaconic acid derivative and fine chemical raw material. Since IAn contains carbon–carbon unsaturated double bonds and active functional groups like anhydride groups, it has become an important functional monomer for the production of polymeric materials. In fact, IAn is a good industrial raw material for manufacturing, for instance, synthetic resins, synthetic fibers, plastics, and nontoxic packaging materials.

In this study, we used the zinc–cobalt DMC (Zn–Co DMC) as a catalyst to introduce IAn into the copolymerization system of CO2 and PO. We can improve the performance of PPC by changing the main chain structure of PPC (Scheme 2).

2 Materials and methods

2.1 Materials

Zinc oxide (ZnO, 99.99%), zinc chloride (ZnCl2, 99%), and potassium hexacyanocobaltate (K3Co(CN)6, 98%) were used; liquid PO was distilled over calcium hydride (CaH2) and stored under nitrogen (N2) gas; CO2 was 99.99% pure, and it was used without further purification; analytically pure IAn was used; the Zn–Co DMC catalyst was prepared according to literature directions (26); and the other reagents were analytically pure and used as received.

2.2 Preparation of Zn–Co DMC catalyst

The literature was referred for configuration (26). The temperature was controlled at 40°C during the entire configuration process. Solution 1 was prepared by dissolving
1.72 g of K$_3$[Co(CN)$_6$] in 20 mL of distilled water. Solution 2 was prepared by dissolving 8 g of ZnCl$_2$ in a mixed solvent comprising 10 mL of distilled water and 10 mL of tert-butanol. Under vigorous stirring, solution 1 was slowly dropped into solution 2 over a period of 30 min; the obtained mixture was then stirred vigorously for a further 1 h to fully complex the ligand tert-butanol with the precipitate. The precipitate was separated from the supernatant by centrifugation, and the residue thus isolated was slurried in a mixed solution of distilled water and tert-butanol (1:1 v/v) and stirred for 1 h, and this step of slurring and stirring was repeated three times. Finally, the precipitated slurry was placed in pure tert-butanol, and the precipitate was separated from the supernatant. The resulting Zn–Co DMC catalyst was dried under vacuum at 60°C for 12 h.

2.3 Terpolymerization of PO, IAn, and CO$_2$

The autoclave was turned on to a temperature of 100°C and allowed to dry in these conditions for 2 h. It was then allowed to cool to room temperature, and the Zn–Co DMC catalyst (0.1 g) and a certain proportion of IAn were placed into the autoclave, which was then quickly closed. CO$_2$ replacement air was poured into the kettle, and this step was repeated two to three times; PO was then poured into the kettle before the liquid port was quickly closed. The pressure was controlled to a value of 4 MPa; the temperature was set to 60°C and the rotation speed to 300 rpm. The reaction was terminated after 24 h. The product was dissolved in chloroform, and the resulting solution was stirred magnetically for about 15 min and then washed and separated with 5% HCl solution and deionized water in turn; this step was repeated three to five times to remove any residual DMC. After centrifugation, the resulting chloroform solution of the copolymer was placed in a round-bottom flask and concentrated under reduced pressure in a rotary evaporator. After being concentrated to a certain concentration, it was precipitated with absolute ethanol, and a small amount of propylene carbonate was removed to obtain the product. The precipitate was then dried under vacuum at 60°C for later use to obtain a terpolymer of CO$_2$, PO, and IAn (PPCIAn).

2.4 Characterization and measurements

Fourier-transform infrared (FT-IR) spectra were recorded using an FTS3000 infrared spectrometer from DIGILAB, USA; notably, FT-IR samples were prepared by the potassium bromide tableting method. $^1$H-NMR spectra of the polymer were recorded using an American Varian INOVA 400M superconducting nuclear magnetic resonance instrument; deuterated chloroform was used as the solvent, and tetramethylsilane was used as the internal standard. The molecular weight of polymer samples and the relevant distribution were determined using the United States Waters GPC2000 high-temperature gel permeation chromatograph, using tetrahydrofuran as the eluent; the flow rate was 1 mL·min$^{-1}$, and the analyte concentration was 5 mg·mL$^{-1}$. A PerkinElmer TGS-2 thermogravimetric analyzer was used to conduct thermogravimetric analysis of the samples; the samples were heated at a rate of 10°C·min$^{-1}$ in an N$_2$ atmosphere. Specifically, under an N$_2$ atmosphere (flow rate: 30 mL·min$^{-1}$), the samples were heated from 30 to 600°C at a rate of 10°C·min$^{-1}$. The specific surface area (SSA) of the DMC catalyst was measured by the nitrogen adsorption method using a Tristar II (3020) physical adsorption analyzer (Mike Instruments Inc). Using a D8 Advance A25 powder X-ray diffractometer (German Bruker), the X-ray diffraction (XRD) pattern of the catalyst was obtained by Cu Kα radiation. The Mike ASAP2460 (Micromeritics) automatic surface and porosity analyzer were used for the Brunauer–Emmett–Teller (BET) analysis, and Zeiss MERLIN Compact scanning electron microscope (Shanghai New Micro Technology R&D Center Co., LTD) was used for scanning electron microscopy (SEM) analysis.

2.4.1 Differential scanning calorimetry (DSC) analysis

Using a Netzsch-204 thermal analyzer in the range from −50°C to 150°C, temperature range is scanned at a heating rate of 10°C·min$^{-1}$ under N$_2$ atmosphere, and the glass transition temperature ($T_g$) value is the recorded value of the second scan.

The polymeric samples' mechanical properties were measured at 23°C using a Shenzhen New Sansi Universal Material Testing Machine (Model: CMT). First, the polymeric material was pressed into a sheet of 1 mm using a YP-250 semiautomatic pressure forming machine from Shanghai Cima Weili Rafter & Plastic Machinery Co., Ltd (Chezhan Bei Lu, Hongkou District, Shanghai). at 170°C and a pressure of 20 MPa. According to the ASTM E 104 standard, a dumbbell-shaped specimen of 25 mm × 4 mm × 1 mm was manufactured to test its tensile properties. The test was carried out at 23°C, 50 ± 5% humidity, and at a tensile speed of 50 mm·min$^{-1}$. Each polymer was made into five splines for testing, and the obtained results were averaged.

The gel contents of crosslinked polymers were determined in accordance with ASTM D 2765. Briefly, the sample was refluxed in boiling chloroform for 24 h. The insoluble
part was then vacuum dried at 80°C until a constant weight was achieved. The gel content was defined as the weight percentage of the insoluble part of the sample. The data were recorded as the average of three parallel measurements.

3 Results and discussion

3.1 Characterization and analysis of the catalysts

Since Zn–Co DMC is a heterogeneous catalyst, its catalytic mechanism is difficult to investigate. Some scholars have proposed that the tetrahedral zinc structure (Scheme 3) is the ground state of the active center of the catalyst (27). The Cl atom in Zn–Co DMC, as a good leaving group (in the form of the chloride ion, Cl−), is speculated to be easily replaceable by an attacking species, in a process that would trigger polymerization initiation. Tert-butanol has a weak “pre-coordination” with Zn2+ in ZnCl2 solution, which provides surface protection Zn2+ for subsequent reactions (28).

Infrared spectroscopy is a powerful tool to identify the coordination and bonding of cyano groups in metal complexes. The infrared spectrum of the Zn–Co DMC catalyst is reported in Figure A1 (in Appendix). At 2,190 cm−1, the CN group can be used to donate electrons to Co atoms (29), showing a sharp and strong CN− bond stretching infrared band. The absorption peak due to the Co–CN bond bending vibration appears in the low wave number region (500–520 cm−1), and the absorption peak appearing at about 3,300 cm−1 is due to the stretching vibration of the catalyst’s hydroxyl group. Some scholars have confirmed that the structure of Co3+–CN–Zn2+ exists in the Zn–Co DMC catalyst through comparison with the infrared spectra of K3[Co(CN)6]. CN− is not only the σ donor of cobalt but also the electron donor of cobalt (30).

The XRD spectrum of the Zn–Co DMC catalyst prepared in this study is reported in Figure A2. As can be evinced from these data, the prepared catalyst is in an amorphous state. The DMC catalyst exhibited a sharp cubic lattice structure with XRD peaks observed at 2θ values of 17.6°, 23.1°, and 28.3°. No sharp peak lines were observed at 2θ values below 17.4°. Studies have found that the introduction of organic ligands into the catalyst can also reduce the crystallinity and increase the catalytic activity (31). Lee et al. (32) reported that without the addition of the organic ligand, Zn3[Co(CN)6]2·nH2O are regular cubic crystal structure, high crystallinity, and low activity catalytic ring opening, which can be indexed as the cubic space group Fm-3m. The Le-Khac (33) research group prepared DMC with fatty alcohols as ligands and found that the DMC catalyst had the highest activity when tert-butanol was used as the ligand. Huang et al. (34) prepared DMC catalysts with different organic ligands, and the results showed that DMC prepared with tert-butanol as the ligand had the highest catalytic activity. This is because the oxygen atom of tert-butanol has strong electronegativity, and the prepared DMC catalyst has a very high amorphous state and high catalytic activity. In addition, with the increase of ZnCl2 addition, the crystallization of DMC was destroyed, and the crystallinity of the catalyst began to decrease (35).

Herold and Livigni (36) reported that decreases in the level of crystallinity of the DMC catalyst are associated with increases in the catalytic activity of the catalyst. The main reason for this trend has to do with the fact that as the degree of noncrystallinity of the DMC catalyst increases, the ability of the PO monomer to penetrate the structural unit of the DMC catalyst also increases, which in turn promotes the ring-opening polymerization reaction of PO (37). Although the microscopic active structure and working mechanism of heterogeneous DMC catalysts are still elusive, the proposed property of the active center of the DMC catalyst is a combination of “cation” and “coordination insertion.”

In addition to crystallinity and particle size, the main factors affecting the catalytic activity of Zn–Co DMC, the catalyst’s SSA can also significantly affect the catalytic activity of the catalyst. In this context, the BET test was conducted to further investigate the structure of the catalyst. Its results are listed in Table A1; the SSA of the Zn–Co DMC catalyst is 1.23 m2·g−1. The SEM image of Zn–Co DMC is reported in Figure 1; the surface of the catalyst is irregular and fine particles, with a higher SSA.
3.2 Characterization and analysis of polymers

By adjusting the feed ratio of PO and IAn, three kinds of PPCIAn-type polymers were prepared, and their FT-IR spectra are reported in Figure A3.

A characteristic absorption peak due to –OH can be observed at 3,470 cm$^{-1}$, indicating the presence of hydroxyl groups in the copolymers. The absorption peaks at 1,740 and 1,245 cm$^{-1}$ are attributed to the C=O bond stretching vibration in the formed terpolymer and the O–C bond stretching vibration peak in the oxygen hydroxyl group (–O–C=O), respectively. This observation indicates that carbonate units are present in the polymer backbone; in other words, CO$_2$ was successfully inserted into the polymer chain. Absorption peaks due to the symmetric and antisymmetric stretching vibrations of –CH$_2$– are observed at 2,945 and 2,860 cm$^{-1}$, respectively; moreover, the peak observed at 1,411 cm$^{-1}$ is due to the in-plane bending vibration of the methyl group. No absorption peak is visible at 1,800 cm$^{-1}$, which indicates that the cyclic carbonate in the polymer has been removed, as also confirmed by the $^1$H-NMR data reported in Figure A6. Compared with PPC, the FT-IR spectra of PPCIAn exhibit an additional absorption peak at 1,637 cm$^{-1}$, which is attributed to the stretching vibration of an unsaturated double bond, indicating that IAn has been successfully integrated into the molecular chain of PPC.

The $^1$H-NMR spectrum of PPC is reported in Figure A5; $^1$H-NMR (400 MHz, CDCl$_3$) δ (ppm): 4.90 (1H, CH$_2$CH), 4.10 (2H, CH$_2$CH), and 1.23 (3H, CH$_3$). The $^1$H-NMR spectrum of PPCIAn is reported in Figure A6; $^1$H-NMR (400 MHz, CDCl$_3$), in addition to the characteristic peaks of PPC, also has δ (ppm): 5.86 (2H, CHCH) and 2.06 (2H, CHCHCH). This evidence indicates that IAn has been successfully connected to the PPC molecular chain.

As can be evinced from the spectrum in Figure A6, the resonance peaks at chemical shift values of 1.3, 4.2, and 5.0 ppm are attributed to the protons of the CH$_3$, CH$_2$, and CH groups in the carbonate unit, respectively. The resonance peaks at chemical shift values of 5.77 and 6.33 ppm are attributed to the two protons at the end of the unsaturated double bond. Moreover, at chemical shift values in the 3.30–3.75 ppm range, in addition to the resonance peak of methylene protons in IAn, there are also the peaks of weaker ether chains. The resonance peaks at chemical shift values of 2.06 and 5.86 ppm are due to the methyl and methine protons in the citraconic anhydride (CAn) unit, indicating that IAn has undergone isomerization to produce CAn. No triplet peaks due to the possible presence of cyclic carbonate in the polymer were observed at δ = 3.9 ppm, indicating that no cyclic carbonate was left after purification, and that purification had indeed been successful (39).

As can be seen from Table 1, with the increase of IAn, the yield of terpolymer increased in turn, which

Figure 1: SEM micrograph of the surface of the Zn–Co DMC complex catalyst.
was higher than that of PPC, and the highest reached 45.79 g/polymer/gcatalyst, indicating that the addition of a small amount of IAn can improve the yield of polymer. The gel permeation chromatography (GPC) curves of the three polyester copolymers are shown in Figure A4. It can be seen that the molecular weights of PPCIAn1, PPCIAn2, and PPCIAn3 are all about 2.1 × 10^5 g·mol⁻¹, which are all higher than the molecular weight of PPC, especially PPCIAn3, whose molecular weight can reach 2.14 × 10^6 g·mol⁻¹, and the molecular weight distribution is only 1.58.

Since the gel formed after ternary copolymerization of IAn is insoluble in deuterium chloroform, Figures A4 and A5 represent only the GPC and ¹H NMR of the soluble part. Contrary to other reports, this phenomenon proves that the soluble terpolymer PPCIAns have a small amount of IAn access, which also leads to a large increase in the molecular weight of the soluble part of PPCIAns (Table 2).

Fukui index is an effective method to study the electrophilic or nucleophilic reactivity of organic compounds and to determine the active part of the molecule. The carbonyl oxygen, acid anhydride oxygen, and double bond carbon in the IAn molecule are the offensive positions of the electrophilic reaction (38).

As expected, when PO, CO₂, and IAn are copolymerized, once IAn participates in the reaction, it will form units connected to the four CO₂/PO copolymer arms. The random connection of these units produces a crosslinked PPC chain (Figure 2).

The results of the said copolymerization indicate that a gel is indeed formed after the introduction of IAn into the reaction mixture. In fact, as the content of IAn in the reaction mixture increases from being absent to a molecular PO/IAn feed ratio of 20:1, the gel content increases from 0% to 51.2 ± 1.7%, which causes the degree of cross-linking of the polymer to increase. Moreover, alongside the said increase in IAn content in the reaction mixture, the yield of the copolymer was observed to increase by approximately one third (Table 1). Gel content is the main index to measure the degree of polymer crosslinking. Therefore, the addition of IAn is obviously beneficial to improve the yield and molecular weight of the polymer, and the uniform distribution of molecular weight makes the polymer to have better processing characteristics and stable final product properties.

### 3.3 Thermal properties

Chen et al. (40) reported a new type of polycarbonate made by ternary copolymerization of CO₂, PO, and carboxylic acid dianhydride. The obtained polymer has T_d,−5% = 276°C, T_d,max = 294.9°C, and T_g = 45.2°C, and has good thermal properties. Sun et al. (41) used a one-pot method for ternary copolymerization of CO₂, maleic anhydride, and epoxycyclohexene. The resulting polymer has T_d,−5% = 273°C and T_d,max = 355°C and has a high thermal decomposition temperature.

The thermogravimetric analysis curves of the various prepared polymers are reported in Figure 3. As can be evinced from this figure, the values for the 5% thermal decomposition temperature (T_d,−5%) and maximum thermal decomposition temperature (T_d,max) of terpolymers PPCIAns are considerably higher than the corresponding parameters for PPC. With respect to PPC, the T_d,−5% and T_d,max values for PPCIAn2 increased by 80 and 100°C, respectively. The main reason for this observation has to do with the fact that the introduction of IAn changed the structure of the flexible
chain of PPC and the mechanism of its thermal cracking. In fact, the extracyclic double bonds of IAn open to form a crosslinked network with PPC, and the crosslinked polycarbonate carbonate chain limits the melting and separation of the carbonate chain.

The $T_g$ value of the polymer was determined by differential scanning calorimetry. As can be evinced from the data in Figure 4, with the increase of IAn content, the $T_g$ value increased from 42°C for PPCIAn1 to 44°C for PPCIAn3; the glass transition temperature of PPCIAn is 5°C higher than that of PPC. This increase in thermal stability was attributed to the formation of PPC crosslinking network. Indeed, evidence indicates that the introduction of IAn into the copolymerization system of CO₂ and PO greatly improved the thermal stability of PPC. Especially when $n[PO]:n[IAn] = 50:1$, the terpolymer PPCIAn2 is basically stable up to 370°C, indicating that the copolymer PPCIAn2 can be routinely processed in a wide temperature range without considering the thermal decomposition problem. The polymer obtained in this study has better thermal properties than the same type of CO₂ terpolymer and can be applied in more extreme environments, which broadens the application range of PPC.

### 3.4 Mechanical properties and dimensional stability of the polymers

The strain–stress curves of PPC and PPCIAns are reported in Figure 5. Evidence indicates that PPCIAns exhibit higher tensile strength than PPC, and their elongation at break is lower than that of PPC. The PPC chain mainly contains carbonate bonds and a small amount of ether bonds.
bonds (42, 43), with fewer polar groups and less interaction between the chains, so the mechanical strength is lower. The introduction of IAn in the copolymer changed the polymer chain structure and increased the rigidity of the main chain. The tensile strength was observed to reach values of 22.3 and 23.1 MPa for PPCIAn2 and PPCIAn3, respectively, and the elongation at break is reduced to 14.5% with respect to traditional PPC (Figure 6). The tensile strength of the polymer PPCIAns has been significantly improved, reducing the ductility and toughness.

Combined with the change of the gel content with the feed ratio, increase in the gel contents of PPCIAns is speculated to lead to increase in the degree of crosslinking within the copolymer. SEM micrographs of PPC and PPCIAn are reported in Figure A7. The appearances of these micrographs indicate that the polymer obtained after adding the active third monomer IAn to the copolymerization mixture is characterized by a greater degree of crosslinking and a more uniform molecular weight distribution than traditional PPC.

Song et al. (44) conducted research on the synthesis and properties of the terpolymer of CO$_2$, PO, and norbornene dioic anhydride. The maximum tensile strength of the obtained polymer is 10 MPa, the elongation at break exceeds 200%, and the rigidity is weak. Chen et al. (42) introduced the third monomer carboxylic dianhydride in the copolymerization of CO$_2$ and PO to prepare a new type of polycarbonate. The tensile strength reached 37 MPa, and the elongation at break was only about 7%, resulting in a polycarbonate material with strong rigidity and weak toughness.
The highly crosslinked PPCIAns are stronger than most similar polycarbonate materials, are stable at high temperatures, and can withstand high pressures. Therefore, PPCIAn has a wider range of applications.

4 Conclusion

We used Zn–Co DMC as a catalyst to introduce IAn into the copolymerization system of CO₂ and PO and successfully synthesized PPCIAns in one pot. The results of the study indicated that the addition of IAn increased the yield and molecular weight of the polymer; in fact, the highest copolymer yield was 45.5 g\textit{polymer}/g\textit{catalyst}, the highest molecular weight was 2.14 × 10^5 g mol⁻¹, and the narrowest molecular weight distribution had a value of only 1.58. The results of thermal and mechanical performance tests indicated that, in the case of PPCIAns, the \( T_\text{g} \) value of PPCIAns can reach up to 44°C, the \( T_\text{d,5%} \) value can reach 250°C, and the \( T_\text{d,max} \) value is 365°C, which is 100°C higher than the \( T_\text{d,max} \) value of PPC. The tensile strength of the PPCIAn copolymers was determined to reach values as high as 23.1 MPa. Compared with PPC, the obtained PPCIAn terpolymers exhibited higher molecular weights, more uniform molecular weight distributions, and superior thermal and mechanical properties. The evidence collected in this study effectively addresses the current applicability limitations of PPC and expands its application range.

Funding information: This research was funded by the National Natural Science Foundation of China (No. 52073228), the Natural Science Foundation of Shaanxi Province (No. 2019JZ-44), the Xi’an Shiyou University Postgraduate Innovation and Practical Ability Training Project (No. YCS20213152), the Nature Science Foundation of Shaanxi Province, China (No. 2019Q-489, No. 2019JZ-44), the Scientific Research Program of Shaanxi Provincial Education Department (No. 18JK0607).

Author contributions: Data curation: Liang Luo and Wen-Zhen Wang; formal analysis: Liang Luo, Yi-Le Zhang, Li Wang, and Lei-Lei Li; funding acquisition: Wen-Zhen Wang; investigation: Yi-Le Zhang and Sai-Di Zhao; methodology: Liang Luo; project administration: Wen-Zhen Wang; writing – original draft: Liang Luo; writing – review and editing: Wen-Zhen Wang, Li Wang, and Lei-Lei Li. All authors have read and agreed to the published version of the manuscript.

Conflict of interest: Authors declare no conflict of interest.

References


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Appendix

Table A1: Textural properties of the Zn–Co DMC complex catalyst

<table>
<thead>
<tr>
<th>Catalyst system</th>
<th>Pure Zn–Co DMC</th>
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<td>SSA (m²·g⁻¹)ᵃ</td>
<td>1.23</td>
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ᵃThe SSA of the catalysts was obtained from nitrogen gas adsorption experiments and calculated by implementing the BET analysis.

Figure A1: FT-IR spectrum of catalyst Zn–Co DMC complex.

Figure A2: XRD pattern of the Zn–Co DMC complex catalyst.

Figure A3: FT-IR spectra of copolymers PPC and PPCIAns.
Figure A4: Molecular weight ($M_w$) distribution in PPC and PPCIAns.
Figure A5: $^1$H-NMR spectrum of copolymer PPC.

Figure A6: $^1$H-NMR spectrum of copolymer PPCIAn.
Figure A7: SEM micrographs of the surfaces of PPC (a) and PPCIA (b).