

Kinetics of Alternating Copolymerization of Carbon Monoxide with Styrene or *p*-Ethylstyrene

Lili Wang, Yong Chen, Weiguo Gao, and Yongshen Xu*

School of Chemical Engineering and Technology, Tianjin University,
Tianjin 300072, P.R. China

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ABSTRACT

Alternating copolymerization of carbon monoxide (CO) with styrene (ST) or *p*-ethylstyrene (EST), catalyzed by the transition metal Pd (II) complexes, was carried out. The kinetics of alternating copolymerization of ST and EST with CO was investigated. The results show that the copolymerization temperature has a sensitive effect on the copolymerization rate and the catalytic activity in the ST and CO copolymerization system. The copolymerization rate increases with the increase of reaction temperature from 55 to 67°C, and then decreases with further increasing the reaction temperature up to 70°C. The variations of the copolymerization rate with the initial CO pressure were also studied, and the results indicate that initial copolymerization rate increases with decreasing the CO pressure in gas phase. Moreover, the semi-continuous experiments performed at different reaction conditions further confirm that lower CO pressure benefits the copolymerization rate. The structure of EST/CO copolymer was verified by means of Fourier transform infrared (FTIR), elemental analysis (EA), ¹H NMR, and ¹³C NMR methods. The characteristic results indicate that the EST/CO copolymer prepared from *p*-ethylstyrene and carbon monoxide in the presence of palladium (II)/2,2'-bipyridyl catalyst is an alternating copolymer. It is interesting to note that there is a higher initial copolymerization rate under proper lower CO pressure in the EST/CO system, which is similar to that in the ST/CO system. In addition, comparing with two systems, there are higher catalytic activity and shorter catalytic life in the EST/CO system than those in the ST/CO system. The different copolymerization rates between EST/CO and ST/CO systems are attributed to the different nature of α -olefins.

Key Words:

kinetics;
polyketones;
alternating copolymerization;
styrene;
p-ethylstyrene.

INTRODUCTION

The alternating copolymerization reactions of α -olefins and carbon monoxide yielding polyketones have become a very attractive field of research [1,2]. Interests in these polymers stem from their unusual properties, the low cost of mono-

mers, the presence of carbonyl functionality, and the potential for further functionalization along the backbone [3]. The polyketone products are not only low cost thermal plastics but also they are featured by unique chemical and

(*) To whom correspondence to be addressed.
E-mail: yongshen@tju.edu.cn

physical properties. It is well known that α -olefins have different copolymerization activities catalyzed by Pd (II) complexes. The differences are attributed to the diverse structures of α -olefins. Copolymerization activity of ethylene/CO is higher than that of styrene/CO due to regio- and stereochemical control in the process of coordinating and inserting of styrene [1].

The mechanism of the copolymerization is of interest in its own right. The migratory insertion reactions responsible for chain growth, alkyl migration to CO, and acyl migration to olefins are members of a larger class of migratory insertion reactions that constitute key steps of transition metal catalyzed C-C bond-forming reactions in processes such as hydroformylation, hydroesterification, olefin oligomerization, and polymerization [4,5].

The copolymer forms by alternating migratory insertion reactions of carbonyl alkyl and olefin acyl complexes. Sen et al. have proven the viability of these intermediates by initiation of the copolymerization with monocationic palladium alkyl and acetyl complexes [6].

Rival migratory insertion reactions of olefin alkyl and carbonyl acyl complexes do not compete with propagation. Sen et al. have further demonstrated that double carbonylation is thermodynamically very unfavourable and has proposed that the higher affinity of palladium for CO relative to ethylene inhibits multiple ethylene insertions [7,8].

An alternative mechanism involving palladium carbene intermediates has been proposed to account for the isolation of a spiroketal polymer from these methanol-based copolymerizations [9]. According to this proposal, there has been increasing evidence that the spiroketal isomer forms after the formation of alternating copolymer [10,11].

Most of the literature focuses on the copolymerization mechanism [12-19], few on the copolymerization kinetics. In the present paper, kinetics studies aimed at providing further insight into the influence of monomer structures on the copolymerization reactivity and the formation of a new kind of polyketone are reported. In particular, comparisons between the copolymerization kinetics of EST/CO and ST/CO were studied. The alternating structure of EST/CO produced was characterized.

EXPERIMENTAL

Materials

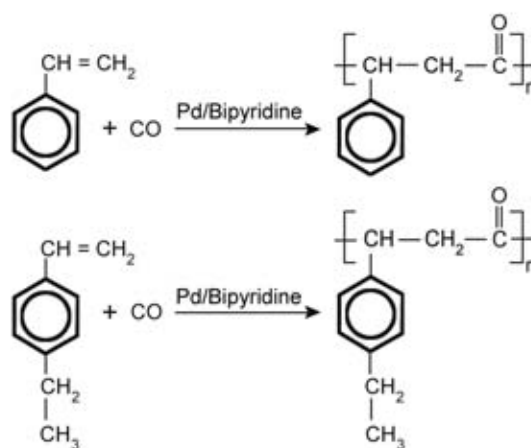
Styrene and *p*-ethylstyrene were dried by CaH_2 and then vacuum-distilled prior to use. Carbon monoxide (>99.95 %) was supplied by Beijing Haipu Industrial Gas Co., Ltd. The other chemicals were purchased from Tianjin Letai Chemical Co., Ltd and directly used without further purification.

Preparation of *p*-Ethylstyrene

p-Ethylstyrene was synthesized in our laboratory [20,21]. Firstly, *p*-ethyl-hyponone was prepared from ethylbenzene by Friedel-Crafts acylation. *p*-Ethyl-hyponone was then reduced and dehydrated to *p*-ethylstyrene. Reduction of *p*-ethyl-hyponone was carried out in a mixed medium of water and methanol where KBH_4 was used as reducing agent. Successive dehydration was catalyzed by KHSO_4 as dehydrating agent through a reaction-rectification process.

Batch Copolymerization Process

The batch copolymerization reactions were preceded in a stainless-steel autoclave (110 mL) equipped with magnetic stirrer. $\text{Pd}(\text{CH}_3\text{COO})_2$, 2,2'-bipyridine, *p*-benzoquinone, styrene (or *p*-ethylstyrene), and methanol were charged in the autoclave, which was then pressurized to the proper pressure with CO at 30- $^\circ\text{C}$ and heated to the appropriate temperature. After a certain time, the reactor was cooled down and the residual gas released. The copolymer, as illustrated in Scheme I, was precipitated and washed with ethanol,



Scheme I. Alternating copolymerization of ST and EST with CO.

and then vacuum dried.

Semi-continuous Copolymerization Process

The semi-continuous copolymerization process was identical to the batch copolymerization process unless that CO is being charged through the overall process to keep CO pressure constant.

Characterization

FTIR was performed by using the KBr pellet technique with Nicolet 5DX Model FTIR spectrometry. The C and H analyses were achieved on an elemental analyzer, PE-2400 Model. ^1H NMR and ^{13}C NMR Spectra were recorded on a Bruker AC-P 200 Model spectrometer. The chemical shifts were referenced to internal tetramethylsilane (TMS).

RESULTS AND DISCUSSION

Copolymerization Kinetics of ST/CO System

Effect of Reaction Temperature on the Kinetics

The copolymerization temperature has a sensitive effect on copolymerization rate and catalytic activity. As styrene and carbon monoxide undergo alternating copolymerization catalyzed by palladium (II) complexes¹, the consumption rate of CO, pressure drop of CO (ΔP) in gas phase, can be used to reflect the copolymerization rate approximately. Copolymerization kinetics curves of ΔP vs. time and catalytic activities at different reaction temperatures are shown in Figure 1 and Table 1.

It shows that copolymerization rate increases with temperature increase. However, it declines in the later period of copolymerization after undergoing a high-rate period at 70°C, which indicates the catalytic life

Table 1. Effect of temperature on catalytic activities in batch copolymerization.

Temperature (°C)	55	60	63	67	70
Catalytic activities (g/g Pd·h)	232	443	469	752	570
Colour of product	white	white	white	gray	gray

Reaction conditions identical to illustrated in Figure 1. The calculation of catalytic activities is based on different reaction times as illustrated in Figure 1.

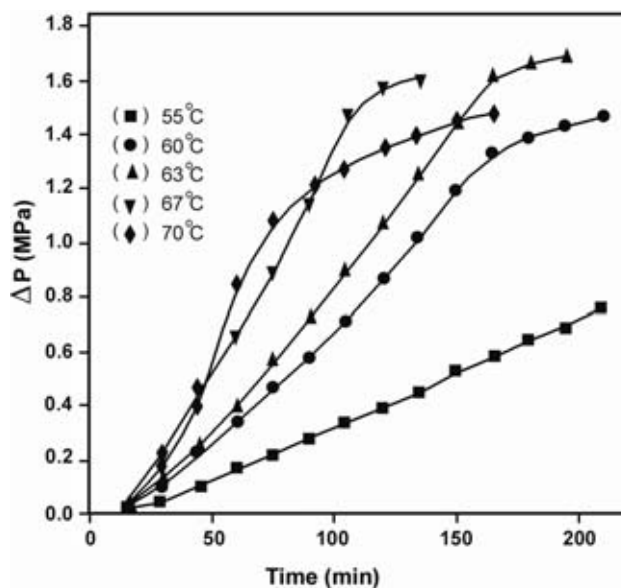


Figure 1. Batch copolymerization kinetics curves at different temperatures. Reaction conditions: palladium acetate, 0.5×10^{-4} mol; 2,2'-bipyridine, 0.175×10^{-3} mol; *p*-benzoquinone, 0.5×10^{-3} mol; ST, 13 mL; methanol, 5 mL; initial pressure of CO, 3 MPa.

of active species is shorter. Copolymer appears gray at higher temperature, partly due to the reduction of Pd (II) to Pd (0). With temperatures lower than 63°C, the copolymerization rates are much lower, but the reaction times are 180 min during which copolymerization process is at almost constant rate. Copolymers produced are white. With temperatures higher than 63°C, however, the reaction times are much shorter (<120 min) during which copolymerization processes are at high rate, even though the copolymerization rates have much higher value. The consumption of monomers is one reason why $\Delta P \sim t$ curves level off soon, the other reason is the thermal decomposition of catalyst at high temperature, which is further confirmed by the fact that products appear gray. A high productivity and white copolymer can be achieved when the copolymerization process is undergoing at 63°C which is proved to be the proper temperature that the thermal decomposition of catalyst can be avoided.

Effect of CO Pressure on the Kinetics

It is known that, the catalytically active species in polyketone formation is thought to be a d^8 square-planar cationic palladium complex L_2PdP^+ , where L_2

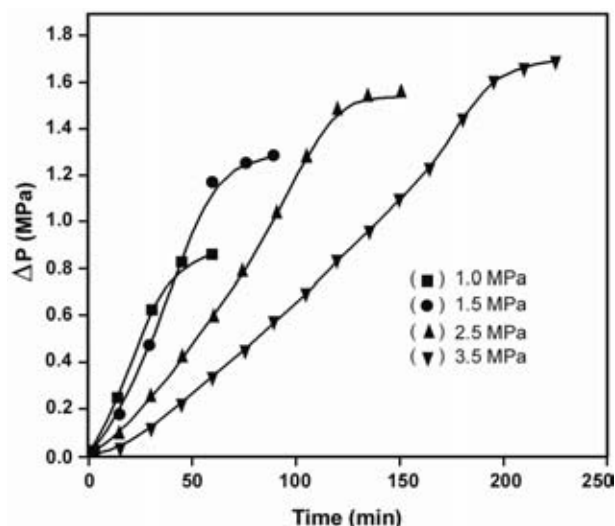


Figure 2. Batch copolymerization kinetics curves for ST/CO. Reaction conditions: palladium acetate, 0.5×10^{-4} mol; 2,2'-bipyridine, 0.175×10^{-3} mol; *p*-benzoquinone, 0.5×10^{-3} mol; styrene, 13 mL; methanol, 5 mL; reaction temperature 63°C .

represents the bidentate ligand and P is the growing polymer chain. The fourth coordination site of palladium (II) may be occupied by styrene (or *p*-ethylstyrene) and carbon monoxide. The two alternating propagation steps are migratory insertion of CO into the palladium-alkyl bond and migratory insertion of styrene (or *p*-ethylstyrene) into the resulting palladium-acyl bond. These two alternating propagation steps make the polymer chain grow. In order to achieve the high copolymerization rate, the relative concentrations of styrene or *p*-ethylstyrene and carbon monoxide in liquid phase need to meet a certain concentration range.

The copolymerization takes place in a sealed autoclave. CO has partition equilibrium in the gas phase and liquid phase under a certain pressure. Therefore, the CO pressure correlates with the concentration of CO in liquid phase where the other monomer ST presents. CO Pressure determines the copolymerization rate according to the above assumption. Figure 2 and Table 2 show the copolymerization kinetics at different CO pressures.

Copolymerization rates can be reflected in terms of the slope of the curves. The slopes of curves rise with the lower initial CO pressure, which indicates that initial copolymerization rate increases with decreasing of CO pressure in gas phase. Lower CO

Table 2. Effect of CO pressure on catalytic activities in batch copolymerization.

CO Pressure (MPa)	1.0	1.5	2.5	3.5
Catalytic activity (g/g Pd·h)	808	858	646	465
Colour of product	white	white	white	white

Reaction conditions identical to conditions illustrated in Figure 2, and the calculation of catalytic activities is based on different reaction times as illustrated in Figure 2.

Table 3. Effect of CO pressure on catalytic activities in semi-continuous copolymerization.

CO Pressure (MPa)	Time (h)	Catalytic activity (g/g Pd·h)
0.5	1.0	486
	1.5	—
	2.0	—
0.7	1.0	1201
	1.5	902
	2.0	719
1.0	1.0	1114
	1.5	984
	2.0	787
1.3	1.0	986
	1.5	926
	2.0	727

Reaction conditions identical to conditions illustrated in Figure 2, and data were obtained by semi-batch copolymerization process.

decreasing of CO pressure in gas phase. Lower CO pressures correlate lower concentration of CO in liquid phase with identical recipe of initial copolymerization in liquid phase. It can be induced from the phenomenon that the lower initial CO pressure is, the higher copolymerization rate is, even though the time that copolymerization rate maintains constant does not last long. So copolymerization rate declines when the CO pressures are lower than a critical value. On the contrary, with the higher initial CO pressure, the copolymerization system can maintain a certain reaction rate for a long time.

In order to further confirm that lower CO pressure benefits copolymerization rate, a group of semi-continuous experiments were performed at constant CO pressures and different reaction times, as shown in

Table 3. To compare with catalytic activity during 1 h, 0.7 MPa of CO pressure is the most favourite. With 1.5-2.0 h, the favourite CO pressure is as low as 1.0 MPa. This means that there are higher initial copolymerization rate under proper lower CO pressures when styrene conversion is also lower. With reaction proceeding, monomers convert to copolymer and equilibrium concentration of CO in liquid phase becomes lower. This brings about higher CO pressure required. Though 0.5 MPa of CO pressure is too low to keep the copolymerization for 1 h or due to the low CO concentration in the liquid phase. Except 0.5 MPa, these contrast to the apparent conclusion that the lower CO pressure is, the higher initial catalytic activity is, as shown in Figure 2. It is difficult to determine the equilibrium concentration of CO in the liquid phase at this temperature and CO pressure. However, it is certain that CO equilibrium concentration in liquid is about 0.118 M/MPa [9], which is much lower than styrene concentration (about 2 M/MPa) in liquid phase, but the perfectly alternating copolymer can be obtained. It is clear that CO coordinates easier on the cavity of palladium (II) reactive species than ST. Rix [3] has concluded that when monomers inserting into the palladium-alkyl/acyl bond, the rate of CO is 2000 times higher than ethylene. Styrene is more difficult than ethylene. With high CO pressure, CO and palladium (II) can form large numbers of stable carbonyl acyl coordinate complexes, which make the catalytically active species in the resting state. That is why low CO pressure seems favourite in the increase of the copolymerization rate.

Copolymerization Kinetics of EST/CO System

Characterization of Copolymer EST/CO in Batch Copolymerization

EST undergoes batch copolymerization with CO under the identical reaction conditions as ST. Figure 3 shows the FTIR spectrum of the copolymer EST/CO. The characteristic strong absorbent peaks of carbonyl group in the backbone of the copolymer are merged at 1709 cm^{-1} and 1695 cm^{-1} . The peak at 3041.4 cm^{-1} is the absorbent peak of unsaturated double bond on phenyl. Two absorbent peaks appear at 1512.9 cm^{-1} and 1608.7 cm^{-1} respectively, which are phenyl characteristic absorbent peaks. The absorbent peak at 823.66 cm^{-1} indicates that styrene has the contrapun

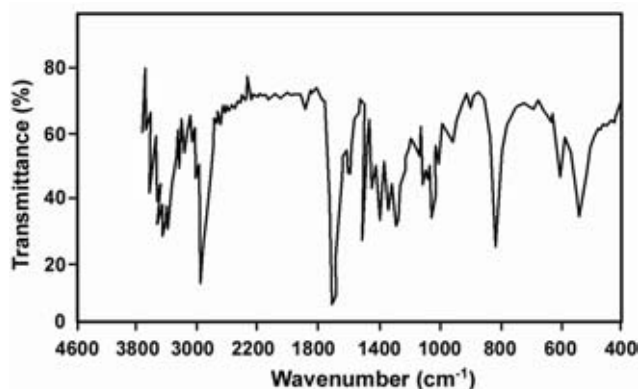


Figure 3. FTIR Spectrum of the copolymer EST/CO.

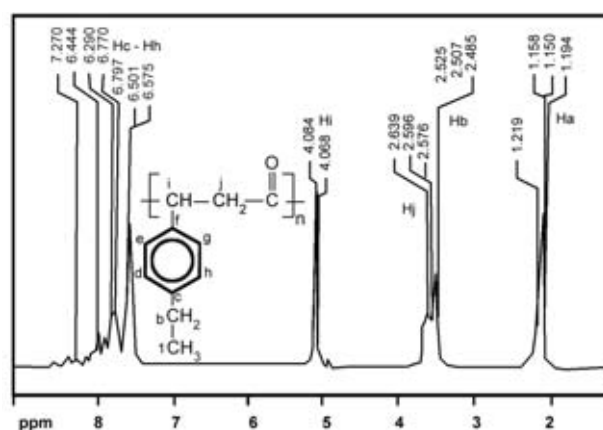


Figure 4. ^1H NMR Spectrum of the copolymer EST/CO.

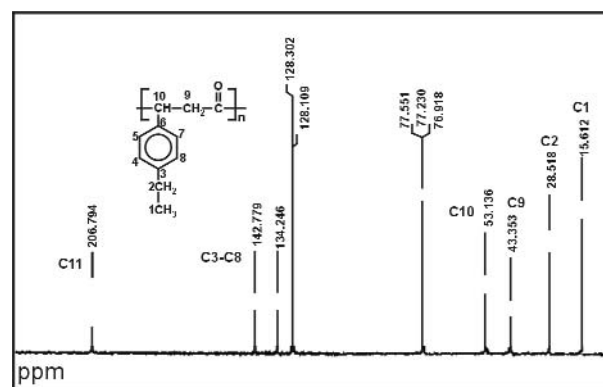


Figure 5. ^{13}C NMR Spectrum of the copolymer EST/CO.

tal substituent group. These absorbent peaks confirm the copolymerization of EST and CO.

^1H NMR and ^{13}C NMR Spectrograms of the copolymer EST/CO are shown in Figures 4 and 5. The peaks at 1.134-1.168 ppm in the ^1H NMR spectrum

Table 4. Elements analysis of EST/CO.

Value	C (%)	H (%)
Theoretical value	82.46	7.55
Experimental value	82.38	7.59
	82.40	7.62

can be attributed to methyl end group. The resonances at 43.353, 53.136, and 206.794 ppm in the ^{13}C NMR spectrum are assigned to backbone methylene, methyne, and carbonyl carbons, respectively, of the repeating molecular unit $-\text{CH}_2\text{CHphCO}-$. The aromatic carbon resonances are located at 128.109, 128.302, 134.246, and 142.779 ppm. The chemical shifts corresponding to the H and C atoms in various chemical environments in the chain of EST/CO confirm the regular structure of alternating copolymer of carbon monoxide and *p*-ethylstyrene.

Table 4 summarizes the C and H analyses results of EST/CO. The experiment values coincide with the theoretical value of alternating copolymer.

The results mentioned above indicate that the copolymer prepared from *p*-ethylstyrene and carbon monoxide in the presence of palladium (II)/2,2'-bipyridyl catalyst is alternating copolymer.

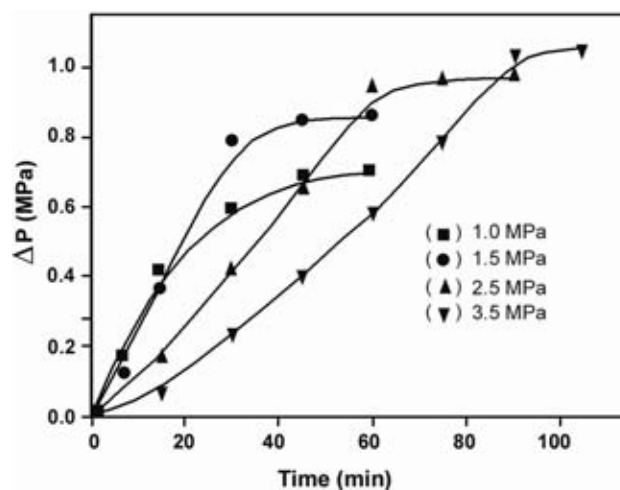
Effect of CO Pressure on the Kinetics

Figure 6 and Table 5 show the results of EST/CO copolymerization kinetics at different CO pressures. The copolymerization rates can also be reflected in terms of the slope of the curves. The results indicate that initial copolymerization rate increases with decreasing of CO pressure in gas phase. However, with the higher initial CO pressure, the kinetics curves seem to be smoother, and the copolymerization sys-

Table 5. Effect of CO pressure on catalytic activities in batch copolymerization.

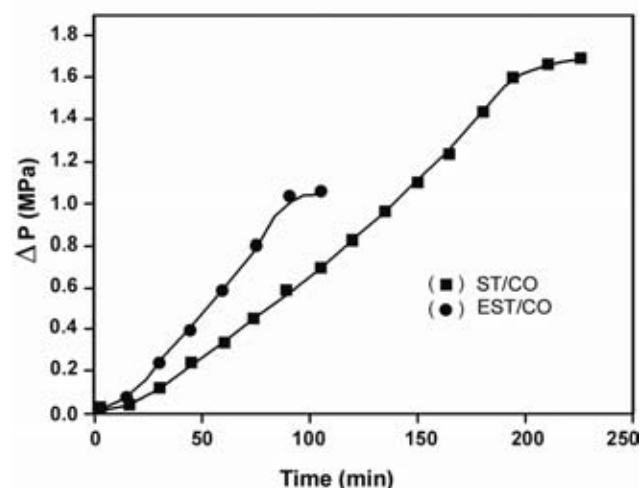
CO Pressure (MPa)	1.0	1.5	2.5	3.5
Catalytic activity (g/g Pd·h)	1429	1272	921	788
Colour of product	white	white	white	white

Reaction conditions identical to conditions illustrated in Figure 6, and the calculation of catalytic activities is based on different reaction times as illustrated in Figure 6.

**Figure 6.** Batch copolymerization kinetics curves for EST/CO. Reaction conditions: palladium acetate, 0.5×10^{-4} mol; 2,2'-bipyridine, 0.175×10^{-3} mol; *p*-benzoquinone, 0.5×10^{-3} mol; styrene, 13 mL; methanol, 5 mL; reaction temperature 63°C.

tem can maintain a certain reaction rate for a long time.

This rule is identical to ST/CO system. In order to compare the copolymerization rates between ST/CO and EST/CO systems, two kinetics curves under identical conditions were picked up in Figure 7.

**Figure 7.** Comparison of batch copolymerization kinetics between ST/CO and EST/CO systems. Reaction conditions: palladium acetate, 0.5×10^{-4} mol; 2,2'-bipyridine, 0.175×10^{-3} mol; *p*-benzoquinone, 0.5×10^{-3} mol; styrene, 13 mL; methanol, 5 mL; reaction temperature 63°C; CO pressure 3.5 MPa.

Copolymerization kinetics show that EST/CO system is more active than ST/CO system, but the life of reactivity in EST/CO system is shorter than that of ST/CO system in the batch copolymerization process. The different copolymerization rates between EST/CO and ST/CO systems are attributed to the different nature of α -olefins. Compared with ST, the electron-donating substitutive ethyl group is introduced into EST on the contrapuntal position of vinyl, which increases the electron cloud density of the double bond of vinyl. This makes EST easier to attack the cavity of cationic palladium (II) complexes, and insert into the growing chain. These two promoting factors make the chain grow rapidly. As ethyl locates on the contrapuntal position of the double bond, the influence of steric effect can be omitted. As a result, EST has the higher reaction activity. However, as it can be seen from the kinetics curves, the copolymerization rate of the EST/CO system levels off earlier than that of ST/CO system. This is maybe due to the specific structure of EST making the crystallinity of EST/CO lower than that of ST/CO, which increases the solubility of EST/CO in reaction medium. Consequently, the viscosity of the EST/CO reaction system becomes much larger. The copolymer slurry produced embeds the catalytic species, which makes it hard for the monomers contacting the catalytic species. This is why the activity of EST is higher than that of ST in early period, but the life of catalyst is shorter.

CONCLUSION

p-Ethylstyrene (EST) and carbon monoxide (CO) can undergo alternating copolymerization in the presence of palladium(II)/2,2'-bipyridine catalyst. The regular structure of EST/CO was confirmed by means of FTIR, EA, ^1H NMR, and ^{13}C NMR methods. Compared with ST/CO copolymerization system, EST/CO copolymerization system has the higher catalytic activities and the shorter catalytic life attributed to the different inherent nature of EST and EST/CO. Factors such as reaction temperature and CO pressure affect copolymerization rates. Optimum reaction temperature and CO pressure are determined, and an appropriately low pressure of CO reaches the maximum copolymerization rate.

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