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Determination of the Number of Active Sites for Olefin Polymerization Catalyzed over Metallocene/MAO Using the CO Inhibition Method

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ABSTRACT: For a determination of the active site concentrations, [C*], the simultaneous kinetics and inhibition method using CO as a catalyst inhibitor were examined. It is noticed that this evaluation method is not quantitatively exact because MAO-activated alkyl Zr sites exist in dynamic equilibrium between dormant states and a chain propagating site and because some CO molecules coordinate even to inactive species. The number of active sites was evaluated on the assumption that two molecules of CO coordinate to each active center. The increase in Al/Zr ratio and temperature increased both the number of active sites and the value of k_p for ethylene polymerization over Cp_2ZrCl_2/MAO. Especially, a drastic increase of activity is mainly due to a much higher value of k_p above a Al/Zr ratio of 2000. A comonomer enhanced drastically the catalytic activity to more than 10 times for ethylene−propylene copolymerization over the *rac*-$Me_2Si(Ind)_2ZrCl_2$/MAO system. This is due to the drastic increase in the propagating rate constant, k_p, rather than the increase in the formation of new active sites by the addition of comonomer.

Introduction

A determination of the number of active sites is inevitable for understanding the kinetics and mechanism of olefin polymerization over Ziegler−Natta catalysts. A knowledge of the number of actual propagating centers, C*, is required so that the appropriate values for the rate constant for chain propagating, k_p, may be calculated from the simplistic equation, $R_p = k_p[C^*][M]$. There are some principal methods which are being used currently for the determination of active center concentrations in both heterogeneous and homogeneous Ziegler−Natta polymerization systems.[1,2] These analyses consist of (1) kinetic and molecular weight studies, (2) quenching methods, (3) radio-tagging procedures, and (4) simultaneous kinetic and adsorption methods.

In this study, we tried to determine the active site concentrations, [C*], by the simultaneous kinetic and inhibition method using CO as a catalyst inhibitor. For a heterogeneous system, these methods have a great advantage because they allow a determination of not only reactive centers but also their distributions due to a close similarity between propagation and inhibition reactions ensuing.[3−6] However, for a homogeneous system one has to be very careful when these chemical methods are applied because active species should be regarded as a dynamic equilibrium between real active and “dormant” states. Chien and co-workers[7−9] have mainly used the technique of radio quenching with tritiated methanol for a determination of the value of [C*] in various MAO-activated metallocene catalysts. Tait and co-workers[10,11] have reported that a reliable estimation of active center concentrations in a homogeneous system, Cp_2ZrCl_2/MAO, can be obtained using the ^{14}CO radio-tagging technique, although this method has been found to be somewhat difficult because the amounts of ^{14}C detected increase as the time of contact, t_c, between the ^{14}CO and the polymerization system increase.

Experimental Section

Materials. Polymerization-grade ethylene and propylene and extra-pure-grade nitrogen were further purified by passing through columns of Fisher RIDOX and 5A/13X molecular sieves. Extra-pure-grade toluene (DongYang Chemical Co.) was further purified by refluxing over sodium metal/benzophenone in a nitrogen atmosphere. Dicyclopentadienyldichlorozirconium (Cp_2ZrCl_2) was purchased from Aldrich Chemical

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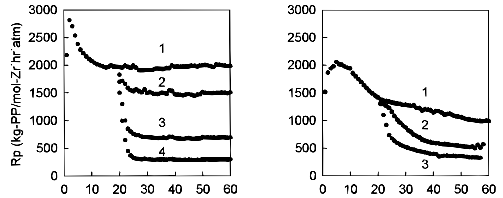
Company, Inc. *rac*-(Dimethylsilyl)bis(indenyl)dichlorozirconium (*rac*-$Me_2Si(Ind)_2ZrCl_2$) was purchased from Witco Co. MAO was purchased from Akzo Co. as a toluene solution. Metallocenes and MAO were used without further purification.

Polymerization. The polymerizations were carried out at the monomer pressure of 1.0 atm (=101.3 kPa) in a 500-mL round bottom flask reactor using a Teflon magnetic spin bar (rugby-ball type which size was 1.3 cm in diameter and 2.5 cm in length). Toluene (300 mL) was introduced into the reactor, the temperature was increased to the polymerization temperature, and then toluene was saturated with the monomer. A prescribed amount of MAO and a given metallocene dissolved in toluene were injected into the reactor by a tuberculin syringe, and then the polymerization was started. The polymerization rate was acquired at 0.01-s intervals from the rate of monomer consumption measured by a hot-wire flow meter (model 820 from Sierra Instrument, the flow rate of which is measurable to 500 SCCM for ethylene gas) connected to a personal computer through an A/D converter. When the ethylene–propylene copolymerization was carried out, the mixture of ethylene and propylene gas was introduced after being mixed at the required mole ratio in a prereservoir. Ethylene and propylene concentrations in the liquid phase were calculated with a computer program for the gas–liquid phase equilibria based on Chao–Seader correlations.[12] Prescribed amounts of carbon monoxide dissolved in toluene were injected during polymerization for the simultaneous measurement of a decrease in the overall rate of polymerization. The carbon monoxide concentration in toluene is 0.76×10^{-6} mol/mL at 25 °C and 1 atm.[13]

Results and Discussion

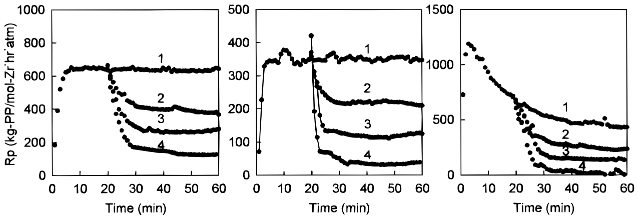
CO Coordination to Metallocene. Before the number of active sites is evaluated for homogeneous metallocene catalysts by means of simultaneous inhibition and the measurements of polymerization rate declined thereafter, we need to consider the validity of this method. MAO-activated metallocene complexes are in dynamic equilibria between active species and "dormant" states.[14–17] Furthermore, there can be many inactive zirconocene species in the Cp_2ZrCl_2/MAO system, for example, Cp_2ZrCl_2 unreacted with MAO, monomethylated $Cp_2ZrMeCl$, dimethylated Cp_2ZrMe_2, and a bimolecular species like $Zr-CH_2-Al$[16] in addition to cationic active species, $[Cp_2ZrR]^+$, suggested by Jordan and co-workers[18,19] and Marks and co-workers,[20] and a dormant state, $[Cp_2ZrRCH_3]$·MAO. These species are expected to be coordinated with CO in a σ-bond only mode due to the electrophilic, high-oxidation state of the early transition metal.[21] The complexation of CO to Cp_2ZrMe_2 and the subsequent migratory insertion had been elucidated to produce $Cp_2ZrMe(MeCO)$.[22] The analogous reaction for $Cp_2TiMeCl$ was found to produce $Cp_2TiCl(MeCO)$.[23]

One should also consider what number of CO are able to coordinate with each real active Zr site. As reported by Guo and Jordan,[21] the reaction of $Cp_2Zr(CH_3)_2$ with 1 equiv of $B(C_6F_5)_3$ under ca. 3 atm of CO in CD_2Cl_2 at 23 °C results in an uptake of 2 equiv of CO and formation of the η^2-acyl carbonyl complex $[Cp_2Zr(\eta^2\text{-}COCH_3)(CO)]-[CH_3B(C_6F_5)_3]$. Accordingly, one should perceive that two CO can coordinate to actual active Zr species and that CO can also coordinate to dormant sites and even to the inactive species indicated above so that the number of active sites cannot be exactly determined from the simultaneous inhibition method. However, a relative degree of formation of the active sites can be measured at certain polymerization conditions. Hereafter, we assumed that two molecules of CO coordinate to one active zirconium site for determination of the number of active sites. In the case of a highly active heterogeneous Ziegler–Natta catalyst, the $Mg(OEt)_2$/benzoyl chloride/$TiCl_4$–$AlEt_3$ system for propylene polymerization and in the $Ti(OBu)_4$/$AlEt_3$ catalyst for ethylene dimerization to 1-butene, the number of active centers has been determined on the assumption that one molecule of CO is adsorbed on each active center.[5,6]



(a) Polymerization conditions; T_p = 50 °C, Zr = 2 μmol, Al = 4 mmol, P_{C2H4} = 1.0 atm, CO/Zr in mol % ;(1) 0 (2) 0.3 (3) 0.6 (4) 0.9.

(b) T_p = 25 °C, Zr = 2 μmol, Al = 4 mmol, P_{C2H4} = 1.0 atm, CO/Zr in mol %;(1) 0 (2) 0.3 (3) 0.6.



(c) T_p = 25 °C, Zr = 4 μmol, Al = 4 mmol, P_{C2H4} = 1.0 atm, CO/Zr in mol %;(1) 0 (2) 0.15 (3) 0.3 (4) 0.5.

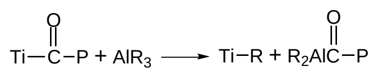
(d) T_p = 25 °C, Zr = 6 μmol, Al = 3 mmol, P_{C2H4} = 1.0 atm, CO/Zr in mol %;(1) 0 (2) 0.1 (3) 0.2 (4) 0.37.

(e) T_p = 0 °C, Zr = 3 μmol, Al = 6 mmol, P_{C2H4} = 1.0 atm, CO/Zr in mol %;(1) 0 (2) 0.15 (3) 0.3 (d) 0.45.

Figure 1. Rate profiles induced by injections of CO after 20 min during ethylene polymerization over Cp_2ZrCl_2/MAO.

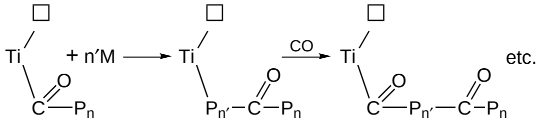
Effects of MAO Concentration and Temperature on the Formation of Active Sites. The decrease in the polymerization rate by CO inhibition was difficult to measure and large errors occur if the monomer consumption rate is very small. In contrast, the stirring limitation occurs due to the higher viscosity of the medium or agglomeration of polymer products during polymerization if the polymerization rate is too high. The adequate consumption rate of ethylene was in the range of 20–50 cm^3/min.

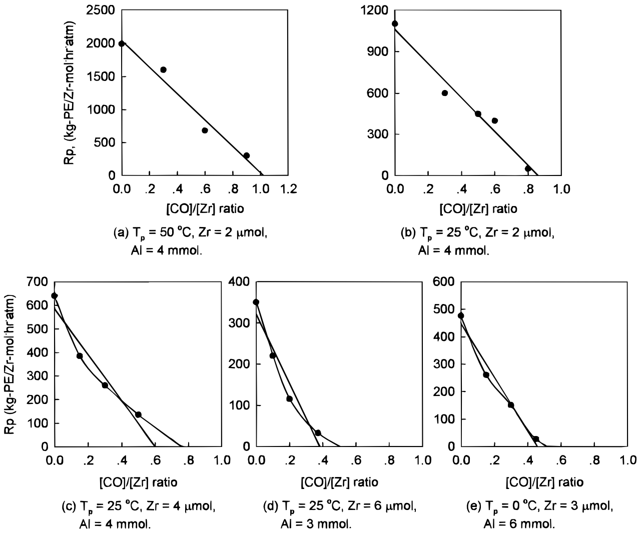
The polymerization rates are sharply decreased to a level which can be determined for a given catalyst after the injection of CO dissolved in toluene (Figure 1). The sudden decreased polymerization rates are not recovered in any polymerization runs over the Cp_2ZrCl_2/MAO system. This kinetic phenomenon is different from that of polymerization over heterogeneous Ziegler–Natta catalysts. The catalytic activity for the heterogeneous catalyst system gradually recovers after a steep decrease in the polymerization rate.[3,5] This recovery of active centers in the heterogeneous catalyst was interpreted in terms of the slow transfer reaction by AlR_3 for a titanium–acyl bond.



$$Ti-\overset{O}{\overset{\|}{C}}-P + AlR_3 \longrightarrow Ti-R + R_2Al\overset{O}{\overset{\|}{C}}-P$$

Also, the polymerization rate recovery occurs because the copolymerization of CO with olefin proceeds as shown in the following.[24]

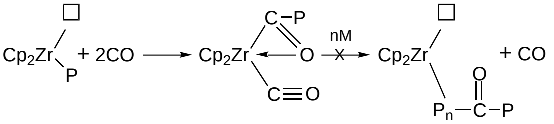




(a) T_p = 50 °C, Zr = 2 μmol, Al = 4 mmol.
(b) T_p = 25 °C, Zr = 2 μmol, Al = 4 mmol.
(c) T_p = 25 °C, Zr = 4 μmol, Al = 4 mmol.
(d) T_p = 25 °C, Zr = 6 μmol, Al = 3 mmol.
(e) T_p = 0 °C, Zr = 3 μmol, Al = 6 mmol.

Figure 2. Decrease in polymerization rates with the amounts of the CO injected. Polymerization conditions are the same as those in Figure 1.

For the Cp_2ZrCl_2/MAO system, however, the eternal decay of polymerization rates implies that two CO molecules coordinate to one Zr site producing the carbonyl complex observed by Guo and Jordan;[21] thus there is no coordinating site for insertion of the ethylene monomer. In other words, the metal–polymer chain cannot regrow in this carbonyl complex.



A species coordinated with one CO is labile and reactive, due to the lack of conventional d → π* back-bonding and the correspondingly weak M–C bonds, and the presence of alkyl or hydride ligands which undergo facile CO insertion.[21] Neither chain transfer reaction nor repropagation of polymer chain occurs because the $Cp_2Zr(\eta^2\text{-COR})(CO)^+$ species is indeed stable so that the polymerization rates did not recover again, as shown in Figure 1.

The decrease of activity (average rate from 10 to 30 min after CO injection) with the amount of CO added was evaluated according to the molar ratio of Al/Zr and polymerization temperature for the Cp_2ZrCl_2/MAO system. Those results are shown in Figure 2. The activity after CO injection linearly decreased with the amount of CO added under the conditions T_p = 50 °C, Al/Zr = 2000 (Figure 2a) and T_p = 25 °C, Al/Zr = 2000 (Figure 2b). While, for the case of T_p = 25 °C, Al/Zr ratio of below 1000 (Figure 2c,d) and of T_p = 0 °C, Al/Zr = 2000 (Figure 2e), i.e., at low temperatures or low Al/Zr ratio, the degree of activity decrease is lessened with the increase in the amount of CO injection. These results might be explained by an equilibrium between a dormant state and real active species, C*. At low MAO concentration and low temperature, this equilibrium reaction goes toward a dormant state or inactive species which can be reconverted to C* reversibly. One of the σ-coordinating sites is vacant in $[Cp_2ZrR]^+$; thus CO, a strong donor of a σ-orbital, coordinates much easier to that cationic species than to other inactive species. Accordingly, if the amount of CO injected was small, most of the CO molecules might preferentially coordinate to real active sites to show the relatively drastic decrease of activity as the amount of CO increases. In contrast, for the case of a large amount of CO, some of the CO molecules coordinate also to dormant and inactive sites, resulting in a slow decrease in the polymerization rate. The increase in MAO concentration and/or temperature makes the equilibrium reaction proceed toward a formation of active sites. Therefore, the activities linearly decrease at even large amounts of CO at high concentrations of MAO and high temperatures.

Table 1. Effect of Al/Zr Ratio and Temperature on the Number of Active Sites in Ethylene Polymerization over the Cp_2ZrCl_2/MAO System[a]

amt of Zr (μmol)	amt of Al (mmol)	Al/Zr	T_p (°C)	$[M]^b$ (mol/L)	mol % of C* [c]/ mol of Zr	k_p $(M\ s)^{-1}$
2	4	2000	50	0.066	52	572
2	4	2000	25	0.098	43	338
4	4	1000	25	0.098	40 (30)	159
6	3	500	25	0.098	25 (19)	147
3	6	2000	0	0.145	31 (23)	142
		11000	70		100[d]	1670
		1100	70		84[d]	168

[a] Polymerization conditions: ethylene pressure = 1.0 atm (=101.3 kPa), solvent = toluene (300 mL), polymerization time = 1 h. [b] Calculated from Chao–Seader's program for phase equilibrium. [c] Extrapolation for 100% drop of rates versus the 2-fold amount of CO injection shown in Figure 2. The values in parentheses are evaluated by linear plot. [d] Cited from ref 25. Determined by the radio-tagging method using CH_3OT.

On the grounds of the assumption that two molecules of CO coordinate to each active center, the number of active centers has been evaluated by extrapolation of the plots of drop in rate versus the amount of CO added to 100% drop in polymerization rate after CO injection. Table 1 summarizes the concentration of active sites of Cp_2ZrCl_2/MAO catalyst together with the rate constant for chain propagation, k_p, calculated from the relation that the overall polymerization rate, R_p, is given by the simplistic equation, $R_p = k_p[C^*][M]$. The number of active centers, C*, increased with the MAO concentration and temperature. The rate constant, k_p, did not increase with the increase in MAO concentration below the Al/Zr ratio of 1000 while it largely increased above 2000. There seems to be a clue about the question of why such a huge excess of MAO is required to obtain high catalytic activity although its mechanism is still unanswered. The increase in activity with the increase in Al/Zr ratio above 2000 is probably due to the drastic increase in k_p values rather than due to the increase in the concentration of an active center.

As mentioned earlier, it should be noticed that the number of active centers evaluated in terms of CO inhibition and the consequent decay of polymerization rate contains all kinds of species which are feasibly coordinated to CO molecules. Conclusively, the trend in the concentration of active sites with the MAO concentration and temperature can be observed although a kinetic study of CO coordination to many feasible zirconocene species needs to be carried out.

Number of Active Sites in Ethylene–Propylene Copolymerization over *rac*-$Me_2Si(Ind)_2ZrCl_2$/MAO Catalyst. Comonomer enhancement of the polymerization rate (R_p) usually exists in ethylene–α-olefin copolymerization for most *ansa*-metallocene-catalyzed systems as well as the heterogeneous Ziegler–Natta catalyst. Activity is also usually enhanced by the addition of comonomer. In spite of the technological and

Table 2. Activities of Ethylene−Propylene Copolymerization over the *rac*-$Me_2Si(Ind)_2ZrCl_2$/MAO System[a]

amt of Zr (μmol)	amt of Al (mmol)	amt of propylene in feed (mol %)	v_{max}[b] (SCCM)	A[c]
60	6	0	54	65
7.2	0.7	25	8	70
16	1.6	25	30	125
60	6	25	>500[d]	
12	1.2	50	15	65
20	2	50	38	150
30	3	50	350[e]	500
12	1.2	75	trace	
24	2.4	75	77	130
32	3.2	75	230[f]	400
20	2	100	trace	
60	6	100	83	80

[a] Polymerization conditions: total monomer pressure = 1.0 atm (=101.3 kPa), temperature = 25 °C, solvent = toluene (300 mL), Al/Zr = 100, polymerization time = 1 h. [b] The maximum consumption rate of ethylene. [c] Average activity for 1 h (unit: kg of polymer/(mol of Zr h atm)). [d] Flow rate was in excess of MF range, and agitation was limited at 5 min. [e] Agitation was limited at 15 min. [f] Agitation was limited at 20 min.

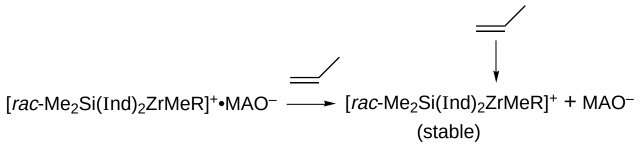
scientific significance of a comonomer enhancement effect, there have been no definite reports on the fundamental explanation of kinetic behavior and the mechanism of copolymerization so far. Several causes of the comonomer enhancement effect are proposed for the polymerization rate under the metallocene/MAO system: (1) physical and diffusional phenomena, (2) the increase in the number of active sites, and (3) the triggering effect by α-olefin to increase the rate constant of propagation (k_p).[26−29] Here, the number of active sites was measured according to variation of the amount of comonomer in ethylene−propylene copolymerization catalyzed by the *rac*-$Me_2Si(Ind)_2ZrCl_2$/MAO system to observe whether the enhancement of the polymerization rate is due to the increase in the concentration of active sites, [C*], by the comonomer. As mentioned earlier, polymerization conditions should be considered to obtain adequate polymerization rates and their profiles for a measurement of [C*] by means of the simultaneous coordination of CO. From preliminary experimental data, we validated that most of the zirconocene chloride converted to the species which can be coordinated to CO in the case of the Al/Zr ratio above 200 in ethylene homopolymerization over the *rac*-$Me_2Si(Ind)_2ZrCl_2$/MAO system. This convinces us that for *rac*-$Me_2Si(Ind)_2ZrCl_2$/MAO the reactive species for CO coordination are much more numerous than for Cp_2ZrCl_2/MAO under the same concentrations of MAO. The MAO concentration should be adjusted at a Al/Zr ratio of 100 to obtain the ethylene consumption rate of ca. 40 cm^3/min. Table 2 shows the ethylene−propylene copolymerization activities according to the variation of comonomer mole percent at the various amounts of Zr and MAO adjusted to obtain a Al/Zr mole ratio of 100. There are drastic increases in activities for copolymerization of approximately 10 times the homopolymerization activity of ethylene or propylene at the same polymerization conditions. At all of 25, 50, and 75 mol % of comonomer, monomer consumption rates greatly exceeded the MF range (measuring limitation is 500 cm^3/min in ethylene) and agitation immediately stopped, arising from a sudden abundance of polymer products. Every copolymerization rate decreased and was not reactivated when a prescribed amount CO was injected after 20 min of polymerization in the same manner as ethylene polymerization over Cp_2ZrCl_2/MAO, as shown Figure 1.

Table 3. Variation of the Number of Active Sites as Comonomer Ratio of Feed in Ethylene−Propylene Polymerization over the *rac*-$Me_2Si(Ind)_2ZrCl_2$/MAO System[a]

amt of Zr (μmol)	amt of Al (mmol)	amt of propylene in feed (mol %)	mol % of C* [b]/mol of Zr	k_p $(M\ s)^{-1}$
6	12	0	100	170
60	6	0	32	19
16	1.6	25	48	20
60	6	25	*c*	>100[d]
24	2.4	75	57	6.1
60	6	75	*c*	>80[d]
60	6	100	36	4.0

[a] Polymerization conditions are the same as those in Table 2. [b] Extrapolation for 100% drop of rates versus the 2-fold amount of CO from an evaluation by simultaneous coordination of CO. [c] Not measured. [d] The guessed value from data in Table 2.

The concentrations of active sites and the values of k_p from the relation $R_p = k_p[C^*][M]$ are shown in Table 3. Concentrations of C* were increased by the addition of comonomer. Here, however, it should be noticed that the values of k_p were drastically increased. (Their values should be compared at the same concentrations of Zr and MAO.) Accordingly, the comonomer enhancement effect is mainly ascribed to the drastic increase in propagation rate constant, although some new active centers are formed by the comonomer. We can suggest the increase in the value of k_p by a comonomer is due to the electronic properties of the active species. In other words, active species are stabilized by π-complexation of the comonomer to the σ-orbital of the Zr center.[28] Because the comonomer π-complex is much more stable than the corresponding ethylene π-complex, the dormant centers can be waked up by the addition of longer-chain α-olefin as follows:



Since MAO-complexed dormant species are easily coordinated to CO similar to cation species, the comonomer addition increases the number of cation active species a little bit. Hence, the value of k_p should increase drastically to explain the comonomer enhancement effect.

Conclusion

The number of active sites was determined by means of simultaneous CO coordination and a consequent decrease in rate for the homogeneous MAO-activated metallocene catalyst system. It is important to realize that MAO-activated alkyl Zr sites appear to be in dynamic equilibria between dormant states and a chain propagating site. Furthermore, it should be considered that some CO molecules coordinate even to inactive species because CO is a strong σ-bond donor. However, because CO might be accessible more facilely to an actual active site than to the other zirconium complexes, the number of active centers could be evaluated from the results of the plot of the amount of CO added versus the corresponding decrease in rate using a small amount of CO. The number of active sites was evaluated on the assumption that two molecules of CO coordinate to each active center. It seems reasonable to conclude that the increase of the Al/Zr ratio and temperature increased both the number of active sites and the value of k_p for ethylene polymerization over Cp_2ZrCl_2/MAO. Especially, a drastic increase of activity is mainly due to a much higher value of k_p in the polymerization above the Al/Zr ratio of 2000.

A comonomer enhanced drastically the catalytic activity more than 10 times in the ethylene−propylene copolymerization over the *rac*-$Me_2Si(Ind)_2ZrCl_2$/MAO system. This cause is apparently due to the drastic increase in propagating rate constant, k_p, rather than the increase in the formation of new active sites by comonomer addition.

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