Macromolecules **1999,** *32,* 6003−6007

Photocatalyzed Ring-Opening Polymerization of 1,1,3,3-Tetramethyl-1,3-disilacyclobutane[1,2]

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Received April 6, 1999

ABSTRACT: Photocatalyzed ring-opening polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (TMDSCB) by Pt(acac)$_2$ is reported. Excellent conversion and high molecular weight polymers are produced in the absence of O$_2$. Inhibition experiments reveal the coexistence of both homogeneous and heterogeneous catalytic species. The relative activity of these is discussed and a tentative polymerization mechanism proposed. Pt colloid is proved to be the heterogeneous catalyst by a TEM study.

Introduction

Polycarbosilanes, polymers with silicon and carbon atoms in the backbone, have been of significant interest owing to their potential applications as silicon carbide ceramic precursors. One synthetic route to such polymers is the thermally induced ring-opening polymerization of 1,3-disilacyclobutanes first reported by Knoth.[3] Later studies found this polymerization could be carried out at lower temperatures through the use of various transition metal complexes, with platinum compounds being the most effective.[4] The substantial ring strain energy of the four membered ring, e.g., 17.7 kcal/mol for tetramethyldisilacyclobutane,[5] was believed to be the driving force for this facile process. Such a reaction had not been employed to a great extent until poly(silylenemethylene) (PSM)[6] and a series of substituted PSMs[7] were synthesized in bulk using H_2PtCl_6 as the catalyst, either at 80−100 °C or by refluxing, with the latter lasting hours to days.

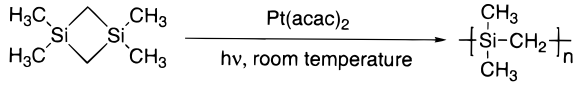
It is well-known that H_2PtCl_6 catalyzes the addition of silicon hydrides to olefins, i.e., hydrosilylation.[8] This may indicate the two processes, ring-opening polymerization of silacyclobutane and hydrosilylation, are similar in some aspects. Moreover, bis(acetylacetonato)platinum(II), Pt(acac)$_2$, was recently reported to serve as a photoactivated catalyst for hydrosilylation addition of silanes to alkenes.[9] Therefore, it became of interest to study the feasibility of activating the ring-opening polymerization process by irradiation.

Herein we report the ring-opening polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (TMDSCB) using Pt(acac)$_2$ as the photocatalyst (Scheme 1). In the absence of O$_2$, polymerization is so efficient that essentially all the monomer is consumed within 15 min and a linear polymer of high M_w (ca. 10^5) is obtained. Inhibition experiments reveal two operative catalytic mechanisms. To the best of our knowledge, such a photoactivated process has not been previously reported.

Experimental Section

Materials. Chloromethylchlorodimethylsilane (Gelest Inc.), Pt(acac)$_2$ (Alfa), 1,7-octadiene (Aldrich), mercury (Bethlehem), THF (anhydrous for monomer synthesis, HPLC grade for GPC measurement, both from Aldrich), dichloromethane (anhydrous, Aldrich), benzene (thiophene free, Aldrich), HPLC grade benzene (Baker), benzophenone (Fisher), and benzhydrol (Baker) were used as received.

Scheme 1



Instruments. Irradiations were carried out on solutions contained in borosilicate glass containers in a Rayonet photochemical reactor equipped with a jacketed beaker (Pyrex). 8 W × 16 RPR-3500 Å lamps from Southern NE Ultraviolet Co. were used. NMR spectra were obtained with a Varian Gemini 200 NMR or a Unity Plus 400 NMR spectrometer and chemical shifts are in ppm with the corresponding deuterated solvents as the internal standard. For the ^{29}Si spectra, TMS was used as an external standard. Infrared spectra were taken with a Galaxy series 6020 FTIR spectrometer. GC/MS measurements were taken on a Hewlett-Packard 5988 mass spectrometer coupled to an HP 5880A GC with a 30 m × 0.25 mm i.d. × 0.25 μm film thickness DB-5 ms column (J&B Scientific). GPC was performed with a HP 1050 series HPLC equipped with a HP 1047A refractive index detector and a PLgel 5 μm mixed-C 300 × 7.5 mm column with a 5 μm guard column. THF was used as eluent. Standard polystyrene samples were obtained from Polysciences. TEM experiments were carried out on a Zeiss EM10 transmission electron microscope using a 400 mesh copper grid coated with carbon purchased from Electronic Microscopy Sciences. UV−vis spectra were measured on a HP 8452A diode array spectrophotometer.

Monomer Synthesis. TMDSCB was synthesized following a literature method[10] and purified by repeated fractional distillation to give a 32% yield. Bp: 116−118 °C/760 mm. ^{1}H NMR (200 MHz, CDCl$_3$, ppm), δ: −0.019 (s, 1H), 0.217 (s, 3H); ^{13}C NMR (APT, 50 MHz, CDCl$_3$, ppm), δ: 2.428, 3.665. ^{29}Si NMR (79.5 MHz, CDCl$_3$, ppm), δ: 2.544. IR (neat, cm^{-1}): 2956, 2901, 1247, 938, 867, 825, 690. MS (EI, 70 eV): 59 (20), 73 (12), 101 (19), 129 (100), 144 (25, M$^+$).

Polymerization. A typical polymerization reaction is described below: Pt(acac)$_2$ (10 μL, 0.025 M in CH$_2$Cl$_2$: 2.5×10^{-4} mmol) was added to TMDSCB (0.5 mL, 0.42 g, 29 mmol) in a 2 mL borosilicate vial. [Since Pt(acac)$_2$ does not dissolve in the monomer, it is necessary to use least amount of methylene chloride for the bulk polymerization.] Benzene, 0.5 mL, was added in the case of solution polymerization. If air was to be excluded from the system, the samples were degassed with argon for 5 min. After irradiation, the sample was kept in the dark for a prescribed period of time and then analyzed. Conversion of monomer (NMR) was determined using the ratio of the integration of methyl group in the monomer and to that in the polymer. The effect of inhibitors was tested by adding 10 μL of 1,7-octadiene or a large drop of mercury before irradiation.

10.1021/ma990509i CCC: $18.00

Table 1. Summary of Polymerization Reactions[a]

expt no.	atm	$Pt(acac)_2$/TMDSCB	irradiation time (min)	solvent[b]	other additive(s)	conversion[c] (%)	$10^{-5}M_w$[d]
1	air	8.6×10^{-5}	continuous			92 (24 h)	3.0 (63), 0.16 (37)
2	air	8.6×10^{-5}	15			80 (24 h)	2.4
3	air	8.6×10^{-4}	15			85 (24 h)	6.9 (22), 0.26 (78)
4	air	8.6×10^{-4}	15	benzene (50%v/v)		49 (24 h)	7.3 (38), 0.20 (62)
5	air	8.6×10^{-5}	15		Hg	30 (24 h)	0.90
6	air	8.6×10^{-5}	15		1,7-octadiene	34 (24 h)	1.4
7	air	8.6×10^{-5}	15		Hg, 1,7-octadiene	9 (24 h)	0.3
8	argon	8.6×10^{-5}	15			98 (15 min)	2.6
9	argon	8.6×10^{-5}	15	benzene (50%v/v)		95 (12 h)	3.1
10	argon	8.6×10^{-5}	15		1,7-octadiene	58 (24 h)	1.5
11	argon	8.6×10^{-5}	15		Hg	95 (15 min)	2.5

[a] See text for experimental details. [b] A minimum CH_2Cl_2 was used to dissolve the catalyst. [c] Conversion was based on an ^1H NMR calculation. The values in parentheses describe the corresponding reaction time. [d] M_w was determined by GPC using THF as eluent; Two values were given when two peaks were clearly present in the chromatography, and the values in parentheses are the area percentage of the two peaks.

The sample for the TEM study was prepared as follows: After 15 min of irradiation and another hour of reaction in the dark, a drop of the polymer solution was applied directly to a carbon-coated copper grid. After being immersed in dichloroethane for 5 min and dried for 10 min in a 60 °C oven, the sample was immediately subjected to the TEM experiment. Two other TEM samples were prepared from the reaction mixture; one sample was left unirradiated and the other irradiated for only 15 min of irradiation. Sample handling was the same.

UV−vis spectra were taken on a TMDSCB solution (0.4 M in CH_2Cl_2) by diluting 0.1 mL of the bulk polymerization mixture to 1.5 mL using CH_2Cl_2 in a quartz cuvette at specified times during the continuous irradiation. Air was used as the background. For quantum yield studies the bleaching of the 344 nm absorption band was used to estimate the consumption of $Pt(acac)_2$. Benzophenone−benzhydrol solution in benzene was used as the actinometer.[11]

Spectroscopic data for the polymer are as follows. ^1H NMR (200 MHz, $CDCl_3$, ppm), δ: −0.263 (s, 1H), 0.029 (s, 3H). ^{13}C NMR (APT, 50 MHz, $CDCl_3$, ppm), δ: 2.701, 7.487. ^{29}Si NMR (79.5 MHz, $CDCl_3$, ppm), δ: 0.040. IR (neat, cm^{-1}): 2953, 2898, 1252, 1058, 830, 804.

Results and Discussion

Facile ring-opening polymerization of TMDSCB containing as little as an 8.6×10^{-5} molar ratio of $Pt(acac)_2$ takes place at room temperature with 350 nm irradiation. At this concentration, the absorbance of $Pt(acac)_2$ at 344 nm ($\epsilon = 3.9 \times 10^3$) is ≈ 2 in the 2 mL vial which has an approximate 1 cm optical pathway. In control experiments, the same mixture stays unchanged in the dark for an indefinite period of time. The monomer also undergoes no reaction when irradiated under similar conditions for 2 h in the absence of the platinum compound. Irradiation for 15 min is sufficient to initiate and carry out the polymerization. Continuous irradiation is unnecessary. Clear and viscous polymers are obtained in most of the platinum-catalyzed polymerization cases, and molecular weights of 10^5 are typical for the bulk polymerization. Polydispersity depends on the reaction conditions. The polymer dissolves easily in common organic solvents such as $CHCl_3$ and THF. The ^1H NMR spectrum indicates that the polymer has a linear structure. The methyl and methylene groups all shift upfield about 0.2 ppm as a result of the relief of ring strain resulting from conversion of monomer to polymer. The $Si{-}CH_2{-}Si$ band in the infrared spectrum is shifted from 938 cm^{-1} in the monomer to 1058 cm^{-1} in the polymer, and this is due to the ring-opening as well. The polymerization experiments are summarized in Table 1.

In the presence of air, and during the early stages of reaction, GPC showed only one narrow polymer peak, with a polydispersity between 2 and 3, as well as unreacted monomer. As the reaction proceeds, both consumption of monomer and growth of polymer, as well as the appearance of another polymer peak of lower molecular weight, occur. The areas of the two peaks are given in Table 1. In experiment 2, we observed substantial broadening of the polymer peak and an increase in polydispersity. The two peaks were also not resolved as clearly as in the other cases. When an 8.6×10^{-5} molar ratio of $Pt(acac)_2$ is used, more than 60% of polymer is observed to be of higher molecular weight. However, with 10 times more catalyst, an inversion of the relative ratio of the two polymer fractions is observed, no matter whether the polymerization is carried out in bulk or in benzene solution (experiments 3 and 4).

When O_2 is excluded from the system (experiment 8), substantial enhancement of catalytic efficiency is observed. Virtually quantitative conversion (98%) to polymer was obtained after only 15 min irradiation. A polymer with high M_w was formed. Careful observation revealed an induction period precedent to rapid polymerization, and a considerable amount of heat released. GPC showed only one polymer peak with a polydispersity around 3 for both bulk and solution phase polymerization under Ar. Solution polymerization in benzene in the absence of O_2 (experiment 9) took longer to reach completion.

The observation of the formation of two polymer peaks on GPC when O_2 is present may indicate that two mechanisms coexist for polymer formation under these conditions. Alternatively, there could be two species of different catalytic activity participating in the formation of polymer.[9b] It is most likely that one of these two species is a homogeneous catalyst, and the other heterogeneous. To understand the nature of these species, mercury and 1,7-octadiene were employed to inhibit polymerization because these inhibitors are known to specifically interfere, respectively, with heterogeneous and homogeneous platinum related catalysts.,[9b,12] Both Hg and 1,7-octadiene show substantial inhibition effects in that they lower both the final conversion and the molecular weight. Figure 1 shows the results of experiments carried out in the presence of air. Only 9% conversion was reached when both inhibitors were added to the reaction mixture, and the molecular weight was almost an order of magnitude lower than found in the absence of these inhibitors. On the other hand, only

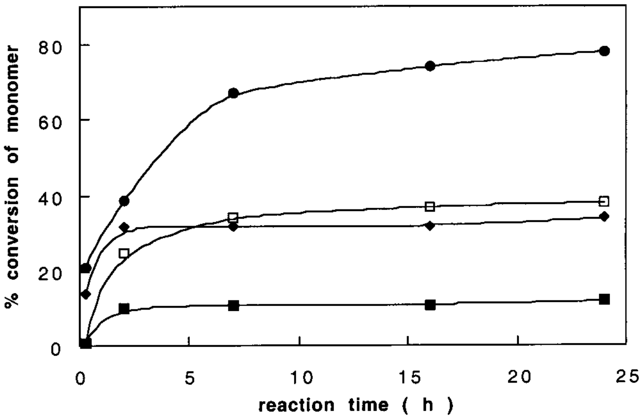


Figure 1. Effect of inhibitors on the conversion of monomer vs reaction time (including 15 min irradiation time) during bulk polymerization in the presence of air: Pt(acac)$_2$/TMDSCB = 8.6×10^{-5}, irradiated for 15 min at room temperature, without any additive (●), in the presence of Hg (◆), in the presence of 1,7-octadiene (□), or in the presence of both Hg and 1,7-octadiene (■).

diene shows an inhibitory effect under Ar. Hg shows no inhibition (experiments 10 and 11, Table 1).

Because homogeneous and heterogeneous transition metal catalysts respond differently to oxygen, the different polymerization behavior we observed gives complementary information about the process. In studying photoactivated hydrosilylation reactions, Lewis and Salvi found that oxygen saturation prior to irradiation nearly completely inhibits the catalytic activity of the proposed homogeneous catalyst formed from Pt(acac)$_2$.[9b] In contrast, it has been suggested that the presence of oxygen is essential to the production and stabilization of the colloidal platinum catalyst.[13] At the same time, many catalysts such as H_2PtCl_6, facilitate both hydrosilylation reactions and the ring opening of disilacyclobutane. We assume, therefore, that the catalysts in our system behave similarly to those that catalyze hydrosilylation. In the presence of O_2, the formation and stabilization of the heterogeneous catalyst is favored, while the activity of homogeneous catalyst is most likely reduced. When O_2 is excluded, heterogeneous catalysis is not likely to take place. Instead, homogeneous catalysis should be dominant. These predictions match, completely, the results of our inhibition experiments. Under aerated conditions, both inhibitors show certain predicted effects, indicating that the two species coexist. However, under inert atmosphere, the heterogeneous catalyst inhibitor, Hg, causes no inhibition, revealing the lack of heterogeneous processes. The activity of the homogeneous catalyst is greatly increased as well, showing the strong effect of O_2. Accordingly, GPC showed two peaks in the polymer region in the former case and only one peak in the latter. These results, when taken together, give a consistent picture of the catalytic process in this system and support the point that, in the presence of O_2, both homogeneous and heterogeneous catalysts are responsible for the polymerization, while homogeneous catalysis dominates under inert atmospheres.

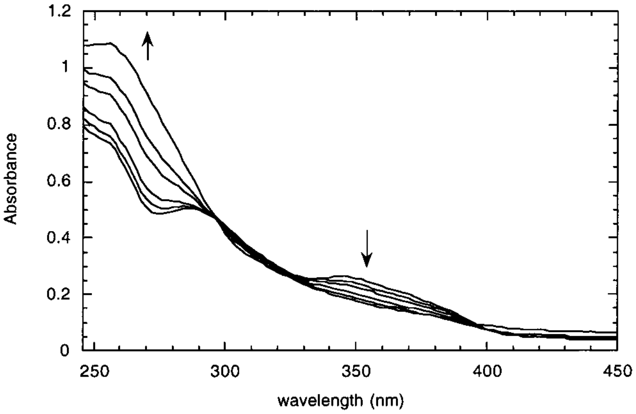


Figure 2. UV–vis spectra change during bulk polymerization in the presence of air. Conditions: 0.4 M TMDSCB in CH_2Cl_2, [Pt(acac)$_2$] = 3.3×10^{-5} M, 350 nm, room temperature, and irradiation time = 0, 10, 20, 40, 60, and 120 min.

To further elucidate the nature of the catalysts, UV–vis spectra were measured during the irradiation a TMDSCB (0.4 M) and Pt(acac)$_2$ (3.3×10^{-5} M solution in CH_2Cl_2) in the presence of air; see Figure 2. During continuous irradiation, the 344 nm band disappears and a new absorption maximum at 258 nm appears. After about 1 h of irradiation, elevation of the baseline is evident and the solution turns yellow. The allowed transition of lowest energy for Pt(acac)$_2$ at 344 nm is assigned mainly to a ligand-localized $\pi-\pi^*$ transition. UV irradiation of the compound in nonreactive solvents results in formation of acetylacetone [H(acac)] and colloidal platinum. Addition of either hydrosilane or olefin accelerates the photodecomposition and a primary photoproduct intermediate (formed via one Pt–O bond cleavage) is observed by both UV–vis and ^{1}H NMR spectroscopy.[14] Subsequent irradiation results in complete loss of one acetylacetonate ligand (two Pt–O bond cleavage) and the formation of a secondary photoproduct **1**, the ultimate active homogeneous hydrosilylation catalyst.[9b] In our case, the decay of the 344 nm peak corresponds to the consumption of Pt(acac)$_2$ and is used to calculate the quantum yield. Similar spectral results were obtained in a previous study.[15] The free protonated ligand, H(acac), has an absorption maximum at 274 nm. We are unable to identify formation of H(acac) because of the proximate 258 nm band which is that of the photoproduct. This is also the active homogeneous catalytic species (we designate it "**P**") that initiates and carries on the polymerization. The exact interaction between the platinum compound and monomer remains unknown. There are several possibililities. Kriner[4e] and Levin[4f] et al. believe a zwitterionic intermediate is the initiating species for the polymerization. If this is the case, coordinative unsaturation of the platinum compound produced upon irradiation may serve to induce electronic redistribution and produce the zwitterion. In other words, the interaction activates the Si–C bond of the four-membered ring. Cundy et al. proposed, based on a study of an analogous reaction of Fe(CO)$_9$,[16b] that oxidative addition to the metal center occurred at the beginning of the interaction.[16a] Recently, oxidative addition products of Si–C bonds of silacyclobutanes to 1-platina-2-silacyclobutane complexes Pt(PEt$_3$)$_3$, **2**, have been isolated.[17] In the Me$_2$Si case, dimerization of the silacyclobutane dominates if phosphine ligand is present, while polymerization is exclusive in the case of the

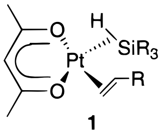


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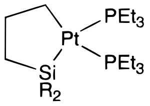
Table 2. Quantum Yield of Disappearance of Pt(acac)$_2$

	additive					
				TMDSCB[c]		
	none	Et_3SiH	1-hexene	0.4 M	1.2 M	6.0 M
$10^3\Phi$	0.047[a]	1.8[b]	2.6[b]	0.19[d]	1.5[d]	10[e]

[a] From ref 15. [b] From ref 14. [c] 350 nm irradiation at room temperature. Decay of 344 nm band is used to calculate the quantum yield, with benzophenone−benzhydrol as chemical actinometer. The molar ratio of Pt(acac)$_2$ to TMDSCB was maintained constant at 8.6×10^{-5}. [d] CH_2Cl_2 as solvent. [e] Bulky polymerization conditions; see text for detail.



R = Ph, Cl, Me

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phosphine-free platinum complexes. In the latter case, presence of an oxidative addition complex was evidenced by NMR. The same interaction also likely takes place between the Si−C bond and photoinduced active platinum species in our system, activating the Si−C bond to facilitate the subsequent chain process.

The quantum yield of disappearance of Pt(acac)$_2$ is reported in Table 2, along with data for the quantum yield in the presence of hydrosilane and olefin. In the case of bulk polymerization (6.0 M), photodecomposition of Pt(acac)$_2$ is at least 2 orders of magnitude more efficient than in its absence. The quantum yield decreases with the decrease of the monomer concentration. In fact, the disappearance of 344 nm band results from the trapping of the coordinatively unsaturated intermediate by TMDSCB. When the concentration of monomer is decreased, the ability to trap the intermediate decreases. Comparison of the quantum yield of TMDSCB (0.4 M in CH_2Cl_2) with quantum yields measured for the case of hydrosilane and olefin under the same concentrations shows that TMDSCB is less efficient than hydrosilane and olefin in promoting the decomposition of the platinum compound. This, in turn, is also a measurement of relative trapping ability.

The elevation of the baseline in the UV−vis spectra and yellowing of the solution are indicative of the formation of colloidal platinum. Moreover, Pt on carbon is known to initiate the ring-opening polymerization.[4b] A TEM study on Pt colloids has been carried out on such systems previously by Lewis.[18] The TEM of our samples carried out on the sample after 15 min of irradiation and 1 h of dark reaction, Figure 3, evidences 0.2−0.6 μm ellipsoids of the right size range for such a colloid. Elevation of the baseline in the visible region and yellowing of the solution were also both evident. However, we observed no such ellipsoids in the reaction mixture with no irradiation, nor in the reaction mixture immediately after 15 min of irradiation, suggesting the heterogeneous catalyst is indeed colloidal platinum, Pt^0, and was produced at later stages of the reaction.

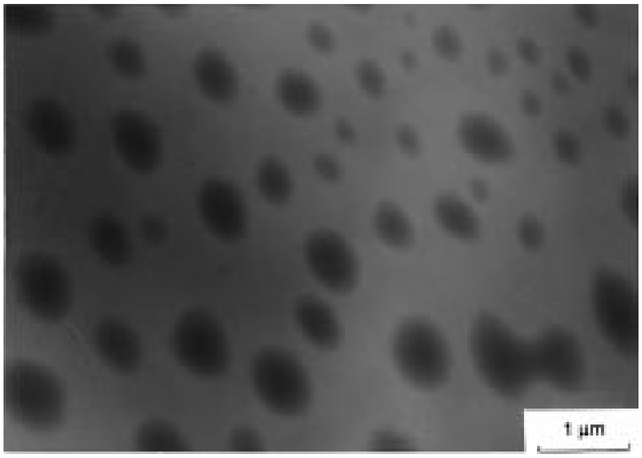
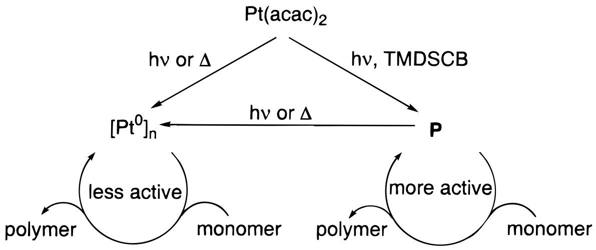


Figure 3. TEM photograph of a bulk polymerization sample after 15 min of 350 nm irradiation and 1 h of dark reaction. Treatment with dichloroethane and 10 min of 60 °C oven drying were performed before the observation.

Scheme 2



The timing of the formation, and the activity, of the two catalytic species is worth noting. GPC showed only one narrow polymer peak at early stages of polymerization. When Hg was added, rapid initiation of polymerization was unaffected (see Figure 1). What is more, TEM studies showed the absence of Pt colloid at early stages of the reaction. Thus, the two catalytic species are not both produced at the onset of the reaction. UV irradiation produces the active homogeneous catalyst first, which is then converted to the heterogeneous catalyst, that is, we suggest, Pt colloid. It is also reasonable that some of the Pt colloid is produced from Pt(acac)$_2$ directly upon irradiation. However, there is an induction period precedent to this process consistent with the absence of heterogeneous catalyst at the onset of irradiation. These results enable assignment of the two polymer peaks as resulting from the two corresponding catalytic species when we were following the reaction by GPC. Pt colloid is produced later in the reaction and is responsible for the formation of the polymer with lower molecular weight. When an 8.6×10^{-5} molar ratio of Pt(acac)$_2$ is used, the heterogeneous catalyst also consumes less monomer. The superior activity of the homogeneous catalyst is well evident when O_2 is excluded from the system. Therefore, we conclude that the homogeneous catalyst is more active than the heterogeneous catalyst.

We observed the inversion of the relative amounts of the two polymer fractions when an order of magnitude more catalyst was used. This may be due to the concentration effect of the two catalytic species. That is, the direct production of Pt colloid from Pt(acac)$_2$ may be concentration dependent. So, when 10 times more Pt(acac)$_2$ is used, more Pt colloid is produced and this consumes more monomer thus resulting in the inversion.

We propose a tentative mechanism for the polymerization (Scheme 2) that shows the two proposed mechanisms for the ring-opening polymerization. Pt colloid may be produced either from Pt(acac)$_2$ or from photoproduct **P**, either thermally or photochemically. But, from the results of the control reaction, the thermal pathway starting from Pt(acac)$_2$ is less likely.

Attempts to clarify the interactions of the platinum compound and monomer are in progress, as well as studies of the scope of such photoactivated processes.

Acknowledgment. Daniel Schwab in the Biology Department, BGSU, helped with the TEM experiments. Bryan E. Fry (Wacker Silicones) and Andrew Guo (Pittsburg State University) read the manuscript and gave us many helpful suggestions. Support from Argonne National Laboratories and a Fellowship from the McMaster Endowment to X.W. is gratefully acknowledged. Partial support from the National Science Foundation (DMR-9526755) and the Office of Naval Research (Navy N00014-97-1-0834) is gratefully acknowledged.

References and Notes

(1) We dedicate this paper to the memory of Professor J. C. Martin.

(2) Contribution No. 384 from the Center for Photochemical Sciences.

(3) Knoth, W. H., Jr. U.S. Patent, 2,850,514, 1958.

(4) (a) Bamford, W. R.; Lovie, J. C.; Watt, J. A. C. *J. Chem. Soc. C* **1966**, 1137. (b)Weyenberg, D. R.; Nelson, L. E. *J. Org. Chem.* **1965**, *30*, 2618. (c) Nametkin, N. S.; Vdovin, V. M.; Pushchevaya, K. S.; Zavyalov, V. I. *Bull. Acad. Sci. USSR* **1965**, 1411. (d) Poletaev, V. S.; Vdovin, V. M.; Nametkin, N. S. *Dokl. Chem. Proc.* **1972**, *203*, 379. (e) Kriner, W. A. *J. Polym. Sci. A* **1966**, *4*, 444. (f) Levin, G.; Carmichael, J. B. *J. Polym. Sci. A-1* **1968**, *6*, 1.

(5) Genchel, V. G.; Demidova, N. V.; Nametkin, N. S.; Gussel'nikov, L. E.; Volnina, E. A.; Burdasov, E. N.; Vdovin, V. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, 2337.

(6) (a) Wu, H.-J.; Interrante, L. V. *Polym. Prepr.* **1991**, *32*, 588. (b) Shen, Q.; Interrante, L. V. *Macromolecules* **1996**, *29*, 5788.

(7) (a) Wu, H.-J.; Interrante, L. V. *Chem. Mater.* **1989**, *1*, 564. (b) Shen, Q.; Interrante, L. V.; Wu, H.-J. *Polym. Prepr.* **1994**, *35*, 395. (c) Rushkin, I. L.; Interrante L. V. *Macromolecules* **1995**, *28*, 5160. (d) Lienhard, M.; Rushkin, I.; Verdecia, G.; Wiegand, C.; Apple, T.; Interrante, L. V. *J. Am. Chem. Soc.* **1997**, *119*, 12020.

(8) Speier, J. L.; Webster, J. A.; Barnes, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 974.

(9) (a) Oxman, J. D.; Boardman, L. D. Eur. Pat. Appl. 398,701, 1990. (b) Lewis, F. D.; Salvi, G. D. *Inorg. Chem.* **1995**, *34*, 3182.

(10) Kriner, W. A. *J. Org. Chem.* **1964**, *29*, 1601.

(11) Moore, W. M.; Ketchum, M. *J. Am. Chem. Soc.* **1962**, *84*, 1368.

(12) Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavalleye, J.-P. P. M.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* **1985**, *4*, 1819.

(13) Lewis, L. N. *J. Am. Chem. Soc.* **1990**, *112*, 5998.

(14) Lewis, F. D.; Miller, A. M.; Salvi, G. D. *Inorg. Chem.* **1995**, *34*, 3173.

(15) Fry, B. E.; Guo, A.; Neckers, D. C. *J. Organomet. Chem.* **1997**, *538*, 151.

(16) (a) Cundy, C. S.; Eaborn, C.; Lappert, M. F. *J. Organomet. Chem.* **1972**, *44*, 291. (b) Cundy, C. S.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1972**, 445.

(17) Amashita, H.; Tanaka, M.; Honda, K. *J. Am. Chem. Soc.* **1995**, *117*, 8873.

(18) Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228.

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