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Living Radical Polymerization of Methyl Methacrylate with a Rhodium(III) Complex–Organic Halide System in Dimethyl Sulfoxide

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ABSTRACT: The polymerization of methyl methacrylate (MMA) with the rhodium(III) complex dihydrido(1,3-diphenyltriazenido)bis(triphenylphosphine)rhodium(III) [$RhH_2(Ph_2N_3)(PPh_3)_2$] as a catalyst and an organic halide (CCl_4, $BrCCl_3$, or CBr_4) as an initiator in dimethyl sulfoxide (DMSO) was studied. For the CCl_4 initiator system, a kinetic study of MMA polymerization indicated that polymerization follows first-order kinetics with respect to the monomer and that the number-average molecular weight (M_n) of the polymers produced increases in direct proportion to the monomer conversion. Monomer-addition experiments showed that after addition of further MMA, the M_n of the polymers continues to increase in direct proportion to the monomer conversion. These results confirmed that the polymerization of MMA in the CCl_4-initiated system proceeds in a living radical manner. In contrast, the systems involving the bromo compounds $BrCCl_3$ or CBr_4 did not show such a living radical nature. For all these initiator systems, the polymers produced had broad molecular-weight distributions. The catalytic activities are discussed in relation to the reaction product between $RhH_2(Ph_2N_3)(PPh_3)_2$ and DMSO. [doi:10.1295/polymj.PJ2005176]

KEY WORDS Living Polymerization / Free Radical Polymerization / Methyl Methacrylate / Rh(III) Complex / Halomethane / Dimethyl Sulfoxide / Molecular Weight /

Free-radical polymerization is one of the most widely used techniques for producing polymers. However, in conventional radical-polymerization processes, it is rarely possible to control the molecular weight or the molecular-weight distribution of the product. Recently, the chemistry of such less-easily controlled reactions has been changed by progress in transition metal-mediated living or controlled radical polymerization systems that permit the control of molecular weights and their distribution. Such catalyst systems were first reported independently by Sawamoto and his co-workers[1] and Wang and Matyjaszewsky[2] in 1995. Sawamoto and his co-workers reported that methyl methacrylate (MMA) is polymerized homogeneously in toluene in the presence of a carbon tetrachloride–ruthenium complex system, (CCl_4)/$RuCl_2(PPh_3)_3$, and a Lewis acid activator (methylaluminum bis(2,6-di-*tert*-butylphenoxide).[1] Wang and Matyjaszewsky reported the bulk polymerization of styrene in the presence of a system consisting of 1-phenylethyl chloride/CuCl and 2,2′-bipyridyl.[2] Since then, systems based on other low-valent transition-metal complexes of iron(II),[3–16] nickel(II),[17–21] rhodium(I),[22–24] and palladium(II)[25] have been found to be effective in similar living or controlled radical polymerizations. The transition-metal complex plays an indispensable role as a halogen carrier, through a series of consecutive reversible oxidation and reduction reactions involving single-electron transfers.

In a previous paper,[26] the trivalent rhodium complex dihydrido(1,3-diphenyltriazenido)bis(triphenylphosphine)rhodium(III) [$RhH_2(Ph_2N_3)(PPh_3)_2$] in conjunction with CCl_4 was shown to be effective as an initiator system for the polymerization of MMA. Under the conditions used previously, the polymerization of MMA to a very high monomer conversion was not attempted and only incomplete kinetic data were obtained. There have been no previous reports on living or controlled radical polymerizations involving $RhH_2(Ph_2N_3)(PPh_3)_2$.

This paper reports the $RhH_2(Ph_2N_3)(PPh_3)_2$ in conjunction with CCl_4 induces the living radical polymerization of MMA. This initiating system gives polymers with a controlled molecular weight, but with broad molecular-weight distributions ($M_w/M_n > 2$).

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) from Wako Chemicals was washed with a saturated sodium hydrogen sulfite solution to remove inhibitor and then with 10% sodium hydroxide solution. The MMA was dried over anhydrous sodium sulfate, distilled twice over calcium hydride under a reduced pressure of nitrogen, and stored at 253 K. Bromotrichloromethane ($CBrCl_3$) (99+%) from Wako Chemicals and carbon tetrabromide (CBr_4) (99%) from Aldrich were used as re-

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ceived without purification. Carbon tetrachloride (CCl_4) from Wako Chemicals was dried over calcium chloride and double distilled over phosphorus pentoxide (P_2O_5). Dimethyl sulfoxide (DMSO) from Wako Chemicals was distilled twice over calcium hydride under a reduced pressure of nitrogen. Triphenylphosphine (PPh_3) from Wako Chemicals was purified by dissolving it in benzene and pouring the solution into ethanol to precipitate the PPh_3. 1,3-Diphenyltriazene (PhNHN=NPh) from Aldrich was recrystallized from petroleum ether. Dihydrido(1,3-diphenyltriazenido)-bis(triphenylphosphine)rhodium(III) [$RhH_2(Ph_2N_3)(PPh_3)_2$] was prepared according to the literature.[27]

Polymerization

All reactions were performed under nitrogen in a glass tube equipped with a side arm, the inlet of which was fitted with a serum cap and capped by a two-way stopcock.

The general procedure was as follows. The required amounts of the $RhH_2(Ph_2N_3)(PPh_3)_2$ (2.0 mmol) and DMSO (8.9 cm^3) were placed in the glass tube. The tube was then deaerated three times by freeze–pump–thaw cycles to remove oxygen, and nitrogen was admitted to a pressure of 1 atm. A mixture of MMA (1.0 mol) and the initiator (1.0–4.0 mmol) was then introduced through the serum cap by means of a syringe. The total volume of the reaction mixture was thus 10.0 cm^3. The reaction mixture was sealed in the glass tube under nitrogen and the tube was then heated to the desired temperature in a water bath. After the required time, the tube was opened and the contents were dried under a vacuum at 313 K.

Characterization

The monomer conversion was determined gravimetrically. The polymer was dissolved in THF and then the solution was vigorously stirred with activated Al_2O_3 to remove the catalyst. The number- and weight-average molecular weight (M_n and M_w, respectively) and the molecular-weight distribution (M_w/M_n) of the polymer were determined by size-exclusion chromatography (SEC) in THF at 303 K on three styrene–divinylbenzene copolymer particle gel columns (Waters Styragel HR 0.5, HR 4E, and HR 5E) that were connected to a Waters ALC/GPC 201A liquid chromatograph and a Waters R401 refractive-index detector. PMMA standards were used for calibration.

Infrared Spectra Measurement

Infrared (IR) spectra were recorded on a JASCO FT/IR-8000 FT/IR spectrophotometer by the diffuse reflectance method. Powdered KBr was used as the dispersant.

RESULTS AND DISCUSSION

Polymerization of MMA with the $RhH_2(Ph_2N_3)(PPh_3)_2$–Organic Halide System

The polymerization of MMA was first attempted in DMSO solution at 323 K with $RhH_2(Ph_2N_3)(PPh_3)_2$ in the absence of an organic halide: in this case the conversion reached only 5% in 24 h. In the absence of organic halide, $RhH_2(Ph_2N_3)(PPh_3)_2$ was found to be almost inactive for the polymerization of MMA. Under similar conditions, the polymerization of MMA was carried out with $RhH_2(Ph_2N_3)(PPh_3)_2$ as the catalyst and one of three organic halides (CBr_4, $CBrCl_3$, or CCl_4) as the initiator in a homogeneous mixture. Figure 1 shows plots of the monomer conversion with time. All three organic halide initiating system induced a smooth polymerization without an induction phase. The CCl_4 initiating system caused rapid polymerization and the monomer conversion reached 94% after 24 h. The $CBrCl_3$ initiating system produced rapid polymerization similar to that of the CCl_4 initiating system in the early stages, but the polymerization slowed down in the later stages and the monomer conversion reached 89% in 24 h. Similarly, polymerization with the CBr_4 initiating system preceded relatively quickly in the early stages, but leveled off at a monomer conversion of around 50%. Figure 2 shows the M_n and M_w/M_n values of the PMMA samples obtained with $RhH_2(Ph_2N_3)(PPh_3)_2$ in the presence of the three organic halide initiating systems. With the CCl_4 initiating system, the M_n increased in direct proportion to the monomer conversion.

In the $CBrCl_3$ initiating system, the M_n increased with increasing monomer conversion in the early stages, but approached a constant value at higher monomer conversions. Thus, the polymerization is ill controlled under these conditions.

In the CBr_4 initiating system, the M_n is independent of the monomer conversion: this result is in agreement with a conventional free-radical polymerization mechanism. When the halides of bromo-derivatives RBr (CBr_4 or $CBrCl_3$) used as the initiator, Rh(I) complex catalyzes the activation of one of the carbon-bromine bonds in RBr to form the one-electron oxidized species, a Rh(II)Br complex and free radicals (R•:CBr_3• or CCl_3•). In general, bromides are much more reactive than the corresponding chlorides. This Rh(II)Br complex may be reacts with RBr in preference to MMA and converts into irreversible Rh(III)Br complex. Therefore, living radical polymerization is only possible with CCl_4 as the initiator.

Effects of the $[CCl_4]/[RhH_2(Ph_2N_3)(PPh_3)_2]$ Ratio

To clarify the role of CCl_4 in the polymerization of

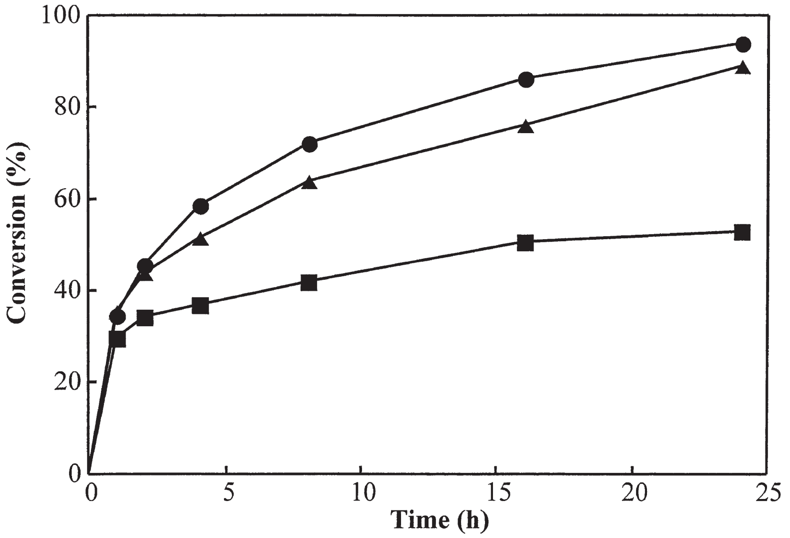


Figure 1. Time-conversion curves for the polymerization of MMA with $RhH_2(Ph_2N_3)(PPh_3)_2$–organic halide system in DMSO at 323 K; [MMA]: 1.0 mol/dm^3; [$RhH_2(Ph_2N_3)(PPh_3)_2$]: 2.0 mmol/dm^3; [Organic halide]: 2.0 mmol/dm^3; Organic halide: CCl_4 (●), $CBrCl_3$ (▲), CBr_4 (■).

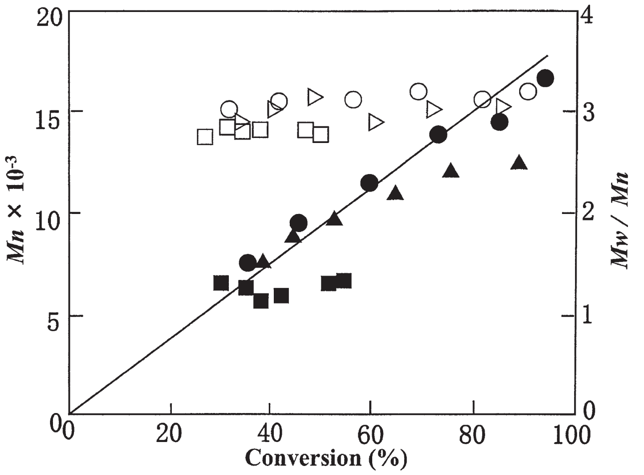


Figure 2. Dependence of M_n and M_w/M_n of PMMA on the conversion in DMSO at 323 K; [MMA]: 1.0 mol/dm^3; [$RhH_2(Ph_2N_3)(PPh_3)_2$]: 2.0 mmol/dm^3; [Organic halide], 2.0 mmol/dm^3; Organic halide: CCl_4, M_n (●), M_w/M_n (○); $CBrCl_3$, M_n (▲), M_w/M_n (△); CBr_4, M_n (■), M_w/M_n (□).

MMA with $RhH_2(Ph_2N_3)(PPh_3)_2$, the ratio of the concentration of CCl_4 to that of [$RhH_2(Ph_2N_3)(PPh_3)_2$] was varied between 2:1 and 1:2, while the ratio of MMA to $RhH_2(Ph_2N_3)(PPh_3)_2$ was kept constant at a value of 500:1.

Figure 3 shows a plot of the monomer conversion with time. At higher concentrations of CCl_4 ([CCl_4]/[$RhH_2(Ph_2N_3)(PPh_3)_2$] = 2:1), the overall polymerization rate was almost the same as in the case of an equal ratio [CCl_4]/[$RhH_2(Ph_2N_3)(PPh_3)_2$] = 1:1, and the monomer conversion reached 98% in 24 h. On the other hand, at a lower concentration of CCl_4 ([CCl_4]/[$RhH_2(Ph_2N_3)(PPh_3)_2$] = 1:2), the polymerization proceeded relatively quickly in the early stages, but slowed down in the later stages and the monomer conversion reached only 70% in 24 h.

Figure 4 shows the M_n and M_w/M_n of the PMMA samples thus obtained. At higher concentrations of CCl_4 ([CCl_4]/[$RhH_2(Ph_2N_3)(PPh_3)_2$] = 2:1 or 1:1), the M_n increased with increasing monomer conversion. On the other hand, at a lower concentration of CCl_4 ([CCl_4]/[$RhH_2(Ph_2N_3)(PPh_3)_2$] = 1:2), M_n increased with increasing monomer conversion up to about 40% conversion, but then became constant. Larger M_n values were obtained at a lower concentration of CCl_4 than at a higher concentration of CCl_4. A [CCl_4]-to-[$RhH_2(Ph_2N_3)(PPh_3)_2$ ratio of 1:1 gave a narrower molecular-weight distribution than that obtained at higher or lower concentrations of CCl_4. Therefore, a [CCl_4]-to-[$RhH_2(Ph_2N_3)(PPh_3)_2$] ratio of 1:1 gives the best control of the molecular weight and its distribution. Table I display the dependence of $M_{n,exp}$ from SEC calibrated versus $M_{n,th}$, calculated by means of following eq 1 for polymerization performed.

$$M_{n,th} = [M]_0/[CCl_4] \times MW_{MMA} \times \text{Conversion} \qquad (1)$$

A linear increase of molecular weight with increasing monomer conversion is observed. However, the obtained molecular weights are lower than calculated value assuming that one molecular of CCl_4 generates one polymer chain. CCl_4 not only serves as an initiator but as a chain transfer agent as well. The deviation of molecular weight is presumably due to the chain transfer reactions.[12]

Living Polymerization with the $RhH_2(Ph_2N_3)(PPh_3)_2$–CCl_4 System

To examine the living radical nature of the poly-

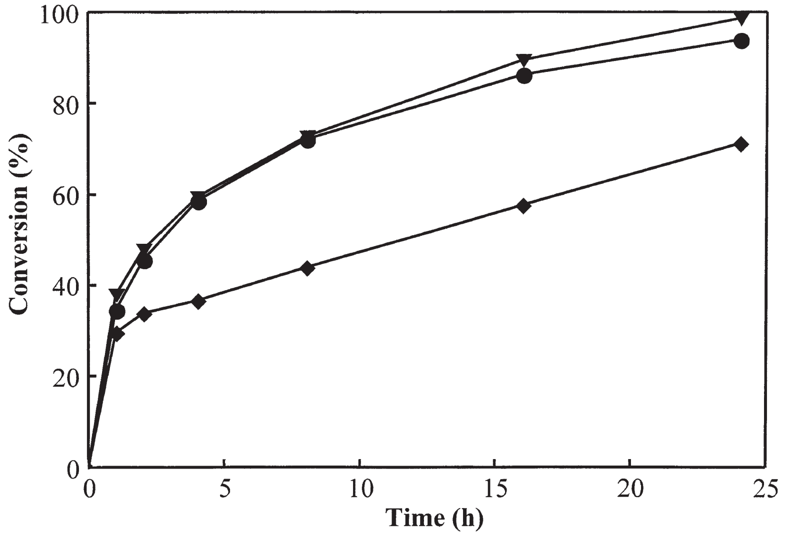


Figure 3. Effects of the $[CCl_4]/[RhH_2(Ph_2N_3)(PPh_3)_2]$ ratio on the polymerization of MMA with $RhH_2(Ph_2N_3)(PPh_3)_2$–CCl_4 system in DMSO at 323 K; [MMA]: 1.0 mol/dm^3; $[RhH_2(Ph_2N_3)(PPh_3)_2]$: 2.0 mmol/dm^3; $[CCl_4]/[RhH_2(Ph_2N_3)(PPh_3)_2] = 2{:}1$, M_n (▼); $[CCl_4]/[RhH_2(Ph_2N_3)(PPh_3)_2] = 1{:}1$, M_n (●), $[CCl_4]/[RhH_2(Ph_2N_3)(PPh_3)_2] = 1{:}2$, M_n (◆).

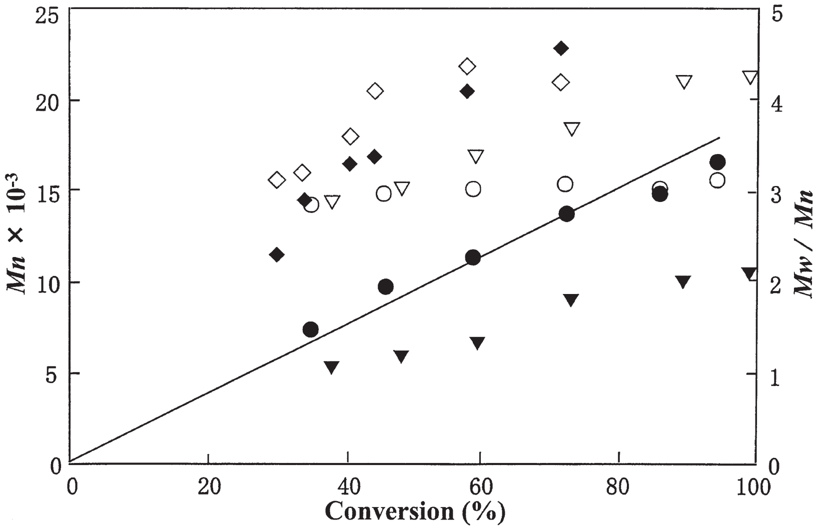


Figure 4. Dependence of M_n and M_w/M_n on the conversion and the $[CCl_4]/[RhH_2(Ph_2N_3)(PPh_3)_2]$ ratio in the polymerization of MMA with $RhH_2(Ph_2N_3)(PPh_3)_2$–CCl_4 system in DMSO at 323 K; [MMA]: 1.0 mol/dm^3; $[RhH_2(Ph_2N_3)(PPh_3)_2]$: 2.0 mmol/dm^3; $[CCl_4]/[RhH_2(Ph_2N_3)(PPh_3)_2] = 2{:}1$, M_n (▼), M_w/M_n (▽); $[CCl_4]/[RhH_2(Ph_2N_3)(PPh_3)_2] = 1{:}1$, M_n (●), M_w/M_n (○); $[CCl_4]/[RhH_2(Ph_2N_3)(PPh_3)_2] = 1{:}2$, M_n (◆), M_w/M_n (◇).

Table I. Dependence of molecular weight of PMMA on the conversion with $RhH_2(Ph_2N_3)(PPh_3)_2$–CCl_4 system in DMSO at 323 K[a]

Time (h)	Conversion (%)	$M_{n,th}$[b]	$M_{n,exp}$
1	34	17000	7200
2	45	22500	9500
4	59	29500	11100
8	72	36000	13600
16	86	43000	14600
24	94	47000	16400

[a]MMA, 1.0 mol/dm^3; $RhH_2(Ph_2N_3)(PPh_3)_2$, 2.0 mmol/dm^3; CCl_4, 2.0 mmol/dm^3. [b]Calculate on the basis of eq 1.

merization of MMA with the $RhH_2(Ph_2N_3)(PPh_3)_2$–CCl_4 system at a $[CCl_4]$-to-$[RhH_2(Ph_2N_3)(PPh_3)_2]$ ratio of 1:1 in DMSO at 323 K. Figure 5 shows the semilogarithmic plot of $\ln([M]_0/[M])$ (where $[M]_0$ and [M] denote the monomer concentrations at time 0 and time *t*, respectively), against time *t*. This plot is linear, indicating that the polymerization is first-order with respect to the monomer and that the concentrations of the active species remain constant during the polymerization.

A volume of monomer equal to the initial volume of the monomer was added to the reaction mixture

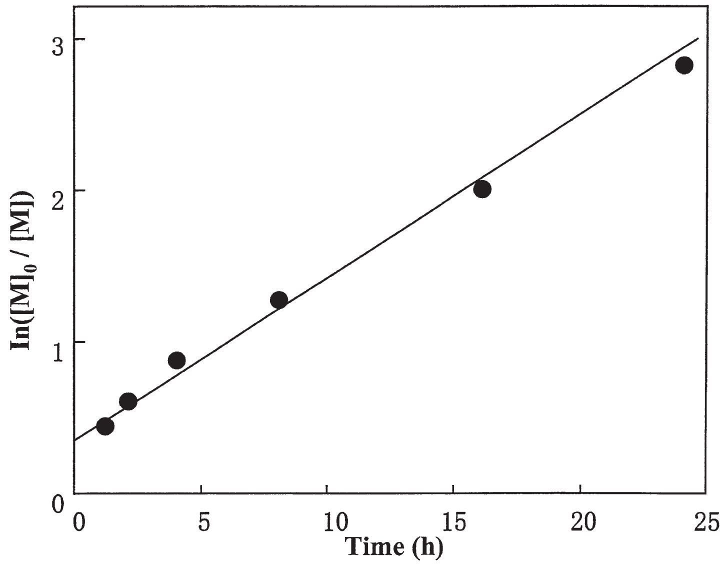


Figure 5. First-order kinetic plot of ln($[M_0/[M]$) versus time for the polymerization of MMA with $RhH_2(Ph_2N_3)(PPh_3)_2$–CCl_4 system in DMSO at 323 K; [MMA]: 1.0 mol/dm^3; [$RhH_2(Ph_2N_3)(PPh_3)_2$]: 2.0 mmol/dm^3; [CCl_4]: 2.0 mmol/dm^3.

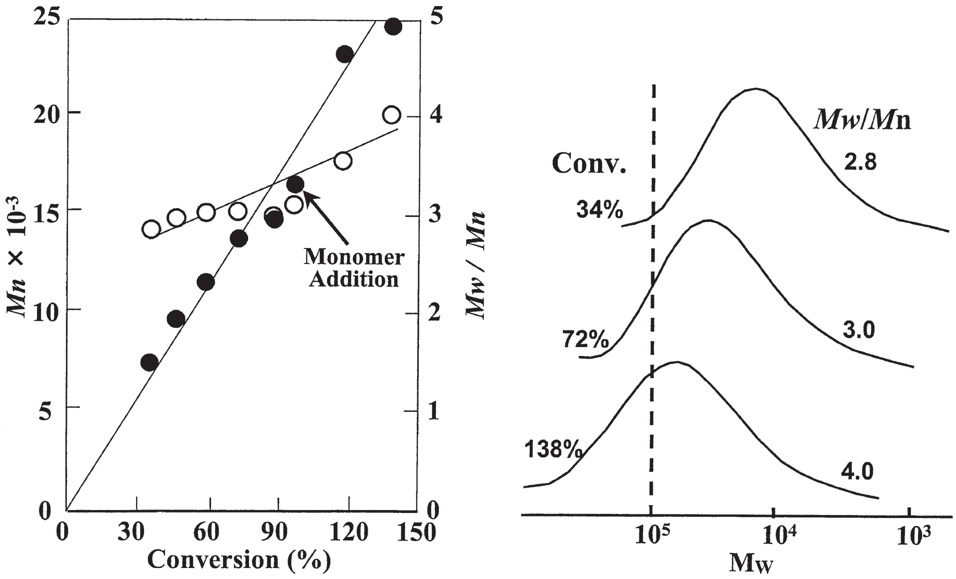
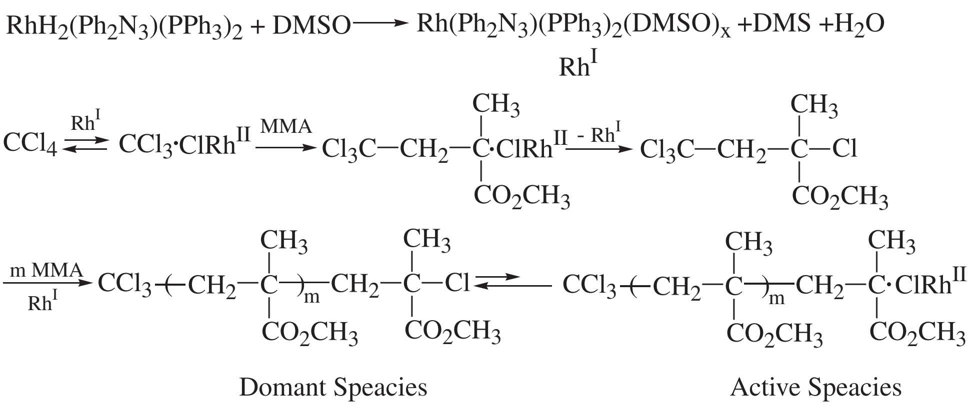


Figure 6. M_n, M_w/M_n and molecular-weight distribution curves for PMMA obtained from monomer addition experiments with $RhH_2(Ph_2N_3)(PPh_3)_2$–CCl_4 system in DMSO at 323 K; [MMA]: 1.0 mol/dm^3; [$RhH_2(Ph_2N_3)(PPh_3)_2$]: 2.0 mmol/dm^3; [CCl_4]: 2.0 mmol/dm^3, M_n (●), M_w/M_n (○).

when the conversion had reached 94% in 24 h and the initial charge of the monomer had been consumed. The added monomer was smoothly polymerized. As shown in Figure 6, after the addition of additional MMA, the M_n of the obtained polymers increased in direct proportion to the monomer conversion and the polydispersity was unimodal. This suggests that polymerization of MMA with the $RhH_2(Ph_2N_3)(PPh_3)_2$–CCl_4 system proceeds in a living fashion. However, the molecular-weight distribution shifted toward a higher molecular weight with increasing conversion, and became broader.

Reaction of $RhH_2(Ph_2N_3)(PPh_3)_2$ with DMSO

These polymerizations are most probably the result of the formation of an active catalyst through reaction between $RhH_2(Ph_2N_3)(PPh_3)_2$ and DMSO, as suggested by the color changes that occurred in the deaerated tube containing $RhH_2(Ph_2N_3)(PPh_3)_2$ in DMSO solution. After deaeration by three consecutive freeze–pump–thaw cycles to remove oxygen from the tube, the color of the solution changed from orange-red to dark greenish brown. When the DMSO was removed under a reduced pressure at 313 K, a dark greenish brown solid residue was obtained. The IR spectrum



x = 1 or 2

DMS = Dimethyl Sulfide

Scheme 1.

of this solid showed bands at 1190, 1281, and 1591 cm^{-1}, which could be assigned to the presence of a monodentate 1,3-diphenyltriazenido ligand,[28] and a band at 1121 cm^{-1} assignable to ν(S–O). It is an established fact[29] that the direction of the S–O stretching mode shift of bonded DMSO in comparison with the free ligand [$\nu(S\text{–}O) = 1055\,cm^{-1}$] always indicates whether coordination has taken place through sulpher or through oxygen donor. From the IR spectrum suggest the sulpher bonded DMSO.[30] The solid showed no IR band ascribable to ν(Rh–H). The IR spectrum indicated that $RhH_2(Ph_2N_3)(PPh_3)_2$ as a Rh(III) complex is converted into the Rh(I) complex, $Rh(Ph_2N_3)(PPh_3)_2(DMSO)_x$ ($x = 1$ or 2). Production of Rh(I) complex can be more favorable at higher concentration of DMSO since sulfoxide ligand is expected to stabilize the lower valent state.[31] Such coordinating solvent–Rh(I) complexes, *e.g.*, [$Rh(Ph_2N_3)(PPh_3)_2\cdot 2THF$] (THF = tetrahydrofuran), have been previously reported.[28]

Mechanism of Initiation of Polymerization of MMA with the $RhH_2(Ph_2N_3)(PPh_3)_2$–CCl_4 System

Among the possible oxidation states of rhodium, which range from +4 to −3, the most common are +1 and +3.[32] A previous paper[33] reports that Rh(I) complexes such as $RhCl(CO)(PPh_3)_2$ induce the radical polymerization of MMA in the presence of organic halides. In the presence of CCl_4, the polymerization of MMA proceeds in an ordinary free-radical fashion. $RhCl(CO)(PPh_3)_2$ is converted into $RhCl_3(CO)(PPh_3)_2$ by oxidative addition of CCl_4, and oxidation states of rhodium changes from +1 to +3. However, $RhH_2(Ph_2N_3)(PPh_3)_2$ induces living radical polymerization of MMA in the presence of CCl_4. When DMSO is used as the solvent, $RhH_2(Ph_2N_3)(PPh_3)_2$ is converted into $Rh(Ph_2N_3)(PPh_3)_2(DMSO)_x$ and the oxidation state of rhodium is changed from +3 to +1. Complexes containing coordinated solvent molecules (solvento-complexes) are themselves often useful as catalysts precursors.[10] $Rh(Ph_2N_3)(PPh_3)_2(DMSO)_x$ is therefore considered to be an active catalyst. A possible mechanism for the polymerization of MMA with the $RhH_2(Ph_2N_3)(PPh_3)_2$–CCl_4 system is shown in Scheme 1. The Rh(I) complex, $Rh(Ph_2N_3)(PPh_3)_2(DMSO)_x$, interacts with the initiator, CCl_4, to form the one-electron oxidized species, a Rh(II) complex. Subsequently, this Rh(II) complex reacts with MMA, followed by the formation of growing radicals. However, the growing radical is reversibly generated from a dormant species with a carbon–chlorine covalent bond, which is derived from CCl_4. During this process, the oxidation state of rhodium undergoes a reversible growing radical one-electron redox reaction from a +2 state to a +1 state, or vice versa. The molecular weight is probably controlled by the growing radical and its dormant counterpart being in an exchange equilibrium that favors the covalent side *i.e.* the concentration of the dormant species is greater than that of the growing radical.[34] The broad molecular-weight distribution of the polymers produced with this initiating system is due to slow interconversion between the radical and dormant species in comparison to propagation. The radicals terminate by either coupling or disproportionation or reversibly deactivated by the Rh(II) complex. Further investigation is required to elucidate the polymerization mechanism.

CONCLUSION

$RhH_2(Ph_2N_3)(PPh_3)_2$ employed as catalyst and CCl_4 as an initiator are effective in initiating the living radical polymerization of MMA to form polymers with a controlled molecular weight. An investigation on the effect of the $[CCl_4]/[RhH_2(Ph_2N_3)(PPh_3)_2]$ ratio on the living radical polymerization of MMA showed that the best control of molecular weight is achieved for the case of $[CCl_4]/[RhH_2(Ph_2N_3)(PPh_3)_2] = 1:1$. Although CBr_4 and $CBrCl_3$ can be used as initiators, the polymers obtained do not have a controlled molecular weight. With all these initiator systems, the polymers produced had broad molecular-weight distributions.

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