Polymerization of Alkyl Methacrylate Catalyzed by Hydridorhenium Complexes

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Hydridorhenium complexes having dimethylphenylphosphine ligands such as $ReH(N_2)(PMe_2Ph)_4$, $ReH(C_2H_4)_2(PMe_2Ph)_3$, $ReH(PMe_2Ph)_5$, $ReH_3(PMe_2Ph)_4$, $ReH_5(PMe_2Ph)_3$ smoothly induce polymerization of alkyl methacrylate in halogenated solvents such as dichloromethane, dichloroethane, chloroform, carbon tetrachloride, and dibromomethane at 30 °C.

Although many ion and radical polymerizations of vinyl monomers have been well documented, examples of polymerization catalyzed by the isolated transition metal complexes are still very limited in spite of their possible controlling ability in activity and selectivity of polymerization. Organolanthanides[1] and early transition metals such as zirconocene/ZnR_2 catalysts[2] have been shown to catalyze living polymerization of methyl methacrylate (MMA). Late transition metals such as iron,[3] ruthenium,[4] cobalt[5] and nickel[6] are also reported to induce polymerization of various vinyl monomers. Recently Sawamoto *et al.* reported living radical polymerization catalyzed by Ru complexes especially in halogenated solvent.[7] Although they recently reported living radical polymerization of MMA by $FeCl_2(PPh_3)_2$ in toluene, this system also requires addition of halogenated compounds.[8] In spite of these previous works, further exploration of new transition metal complexes,[9] which can induce polymerization of vinyl monomers, is still attracting interests, because of their intrinsic ability in highly controlled polymerization processes. In this communication, we wish to describe new polymerization of alkyl methacrylates catalyzed by the isolated rhenium hydride complexes under ambient conditions.

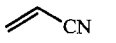
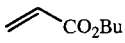
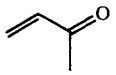
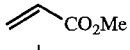
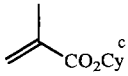
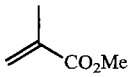
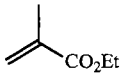
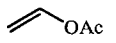
Results of polymerization of MMA catalyzed by rhenium complexes in CH_2Cl_2 at 30 °C are listed in Table 1. All hydridorhenium complexes bearing PMe_2Ph ligands catalyze the polymerization, among which $ReH(N_2)(PMe_2Ph)_4$ (**1**)[10] is the most active catalyst. The hydridorhenium complex with a tridentate phosphine (etp) is far less active for the polymerization and no polymerization took place by $ReCl_3(PMe_2Ph)_3$. It should be noted that polymerization occurs only in halogenated solvents such as dichloromethane, 1,2-dichloroethane, chloroform, carbon tetrachloride, and dibromomethane. Such solvent effect is quite

Table 1. Polymerization of MMA catalyzed by rhenium complexes[a]

Catalyst	Yield / %	Activity / g/mol Re h	M_v[b]
$ReH(N_2)(PMe_2Ph)_4$	33	1,000	63,000
$ReH(C_2H_4)_2(PMe_2Ph)_3$	15	490	135,000
$ReH_3(PMe_2Ph)_4$	15	480	157,000
$ReH(PMe_2Ph)_5$	16	420	122,000
$ReH_5(PMe_2Ph)_4$	27	640	85,000
$ReH_5(etp)$[c]	trace	-	-
$ReCl_3(PMe_2Ph)_3$	0	0	-

[a]Conditions: catalyst = 0.012-0.016 mmol, MMA = 9.36 mmol, in CH_2Cl_2 (2 ml) at 30 °C for 24 h. [b]Determined by viscometry in benzene. [c]etp = $PhP(C_2H_4PPh_2)_3$.

Table 2. Polymerization of Vinyl Monomers by $ReH(N_2)(PMe_2Ph)_4$ (**1**)[a]

Monomer	*e* value	Yield / %	Activity / g/mol Re h	M_v[b]
	1.23	0	0	-
	0.85	trace	-	-
	0.68	0	0	-
	0.64	19.7	560	79,000
	0.41	71.6	2,040	50,000
	0.40	33.3	1,000	63,000
	0.17	29.8	880	-
	-0.22	0	0	-
	-0.80	0.5	20	-

[a]Conditions: catalyst = 0.013-0.015 mmol, monomer = 5.7-15.0 mmol, in CH_2Cl_2 (5.0 ml) at 30 °C for 24 h. [b]Determined by viscometry in benzene. [c]In CH_2Cl_2 (2 ml).

similar to Sawamoto's Ru catalyst system.[7] When the 4:1 toluene/CH_2Cl_2 mixed solvent was used, the yield of poly(methyl methacrylate) (PMMA) slightly decreased (27%). The polymerization proceeded even in the toluene solution (5 ml) containing only 10 μl of CH_2Cl_2, though the yield decreased to 4%.

$ReH(N_2)(PMe_2Ph)_4$ (**1**) catalyzes various vinyl compounds in CH_2Cl_2 at 30 °C as shown in Table 2. Methyl acrylate, cyclohexyl methacrylate, methyl methacrylate, ethyl methacrylate, and styrene were polymerized by **1**, where the observed relation between activity and *e*-values of the monomers is not in accord with the ionic polymerization, but rather suggests radical polymerization. The initiator efficiencies of these catalysts, which were estimated from molecular weight of the polymer and the amount of catalyst used, were in the range of 0.1-0.3. Dispersity of the PMMA (Mw/Mn) estimated from GPC analysis was 1.5-3 and increased with time. Molecular weight of the PMMA increases with increase in the yields (Figure 1), but the

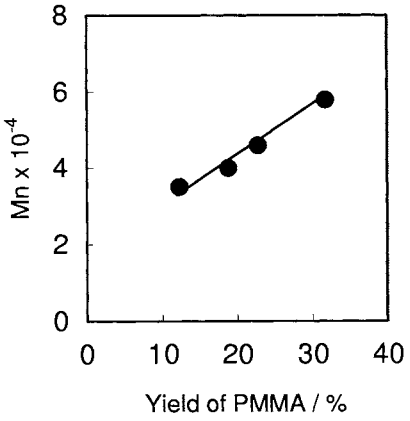


Figure 1. Polymerization of MMA by $ReH(N_2)(PMe_2Ph)_4$ (**1**). Conditions: [**1**] = 2.2 mM, solvent = ClC_2H_4Cl, temp. = 50 °C.

yield gradually levels off, suggesting involvement of slow catalyst deactivation process. From these facts, the present polymerization seems to proceed by fast initiation with slow chain transfer process.

In order to examine the radical character of the propagation end, effect of added radical scavenger was studied. When an equimolar amount of galvinoxyl per **1** was added, the polymerization rate slightly decreased, while no polymerization took place in the presence of 10 times excess of galvinoxyl, suggesting that the polymerization did not proceed by a free radical chain mechanism, but the propagation end may have radical character. Accordingly the copolymerization curve of methyl methacrylate and styrene catalyzed by **1** was quite similar to that of known radical polymerization induced by AIBN (Figure 2).[11]

In order to examine active species in the catalyst solution, ^1H NMR of products recovered from ClC_2H_4Cl solution of **1** was measured, indicating the formation of $ReCl_3(PMe_2Ph)_3$ and some uncharacterized hydride species.[12] Although the isolated $ReCl_3(PMe_2Ph)_3$ was inactive toward the polymerization at all (Table 1), the above solution did catalyze the polymerization of MMA. Probably some of the hydride species may be responsible

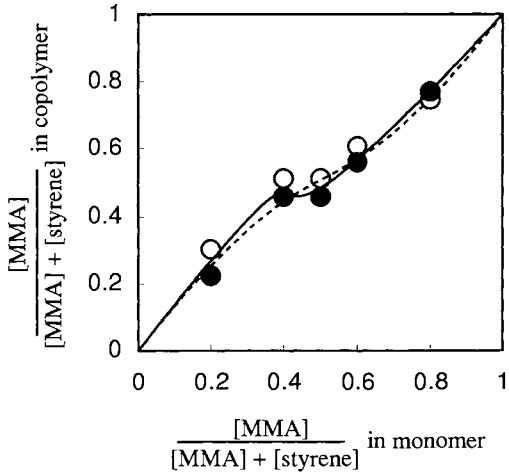


Figure 2. Copolymerization of MMA and styrene by $ReH(N_2)(PMe_2Ph)_4$ (**1**) in ClC_2H_4Cl at 50 °C. Open and solid circles indicate composition in copolymer determined by elemental analyses and ^1H NMR spectra, respectively. The dashed line was taken from radical copolymerization by AIBN at 60 °C.[11]

for the polymerization, however, we should wait for further detail mechanistic study to fully understand this rhenium-catalyzed polymerization process.

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12 ^1H NMR (300 MHz, C_6D_6): Re-H: δ -5.93 (tq, J = 12, 66 Hz), δ -9.55 (tt, J = 22, 97 Hz), δ -13.01 (br).