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Polymerization of *N*-Propargylamides with a Rh−Vinyl Complex: Confirmation of the Presence of Long-Lived Active Species

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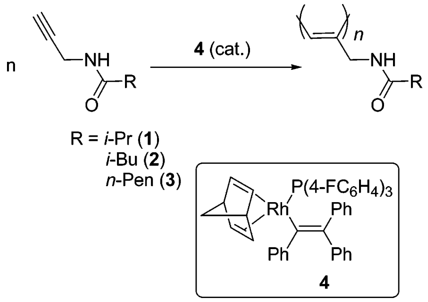
ABSTRACT: The polymerization of *N*-propargylamides ($HC{\equiv}CCH_2NHCOR$, R = *i*-Pr (**1**), *i*-Bu (**2**), or *n*-Pen (**3**)) with a Rh vinyl complex (**4**) was examined. The polymerization of **2** in chloroform in the presence of triphenylphosphine yielded polymer with a relatively narrow molecular weight distribution (M_n = 17 300, M_w/M_n = 1.36). The first-order plot based on the time profile of polymerization at 0 °C was linear, and the second monomer feed was also consumed completely in multistage polymerization. These results indicate that this polymerization has a livinglike nature. Further, a block copolymer was successfully prepared from monomers **2** and **3**.

Introduction

A tremendous amount of research has been performed regarding transition-metal-catalyzed polymerizations including Ziegler−Natta polymerizations[1] and ring-opening metathesis polymerization of cycloolefins,[2] and a wide variety of transition-metal catalysts from group 4 to 9 have been developed for the polymerization of substituted acetylenes.[3] Among these catalysts, Rh catalysts efficiently polymerize monosubstituted acetylenes such as phenylacetylene (PA),[4] propiolic esters,[5,6] and *N*-propargylamides.[7] Rh complexes are capable of inducing the polymerization in protic solvents such as amines,[4a] alcohols,[4b,c] and even water[4d] because of their low oxophilicity to selectively produce stereoregular polymers with cis-transoidal structure.[4b,e,f] The stereoregular polymers give rise to helical conformations[8] with a selective screw sense, upon either incorporation of chiral substituents[4g,6,7] or complexation with optically active compounds.[9] A chiral helical polymer, poly(3-dodecoxy-2,4-hydroxyphenylacetylene), was recently obtained by the polymerization of the corresponding achiral monomer with a chiral Rh-based catalyst system.[10] Further, stimuli-responsive hydrogels[11] and organogels[12] synthesized by the polymerization with Rh catalysts exhibit changes in conformation and morphology in response to external stimuli such as chiral additives, polar solvents, and heat. The polymerization with Rh complexes proceeds by the insertion mechanism,[3,4] instead of the metathesis mechanism which applies to early-transition-metal catalysts.

Neither chain transfer nor termination reactions occur in living polymerizations. It is possible in living polymerization to control the molecular weight by adjusting the initiator-to-monomer ratio and to achieve narrow molecular weight distribution (MWD). Falcon et al. have reported that PA polymerization with $[(nbd)Rh(OCH_3)]_2$/dppb (nbd = 2,5-norbornadiene, dppb = $Ph_2P(CH_2)_4PPh_2$) proceeds in a living fashion to give poly(PA) with small polydispersity (M_w/M_n < 1.1).[13] The initiation efficiency is below 1% due to the formation of various species from the mixture of $[(nbd)Rh(OCH_3)]_2$ and dppb. Kishimoto et al. have achieved the living polymerization of PA using two catalyst systems, i.e., $Rh(C{\equiv}CPh)(nbd)(Ph_3P)$/4-$Me_2NC_5H_4N$ (DMAP)[14] and $[(nbd)Rh(OMe)]_2/Ph_3P$/DMAP,[15] both of which require the addition of DMAP and in which the initiation efficiency is 37% and 73%, respectively. We have reported that the $[(nbd)RhCl]_2/Ph_2C{=}C(Ph)Li/Ph_3P$ ternary catalyst system[16] and the Rh−vinyl complex isolated from this ternary catalyst system[17] polymerize PA and its derivatives in a living manner with quantitative initiation efficiency. However, all of these Rh catalyst systems induce living polymerization only for PA and its derivatives. The present article deals with the polymerization of *N*-propargyl-2-methylpropanamide (**1**), *N*-propargyl-3-methylbutanamide (**2**), and *N*-propargylpentanamide (**3**) with a Rh−vinyl complex (**4**), confirmation of the presence of long-lived active species, and block copolymerization of monomers **2** and **3** (Scheme 1).

Scheme 1



Experimental Section

Materials. $[(nbd)RhCl]_2$ (Aldrich), $(4\text{-}FC_6H_4)_3P$ (Aldrich, 98%), Ph_3P (WAKO, 97%), $(4\text{-}CH_3C_6H_4)_3P$ (Aldrich, 98%), $(4\text{-}CH_3OC_6H_4)_3P$ (Aldrich, 95%), Bu_3P (Aldrich, 95%), and $(C_6H_5O)_3P$ (TCI, 95%) were commercially obtained and used without further purification. THF as polymerization solvents was distilled from sodium/benzophenone, and other solvents were distilled twice from CaH_2. *N*-Propargylamides (**1**−**3**) were prepared by the condensation of the corresponding acyl chlorides with propargylamine in the presence of pyridine in ether.[7b] Rhodium complex **4** was synthesized according to the literature.[17]

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Table 1. Polymerization of *N*-Propargylamides 1−3 with Rh Complex 4[a]

			polymer[b]		
run	monomer	solvent	yield, %	M_n[c]	M_w/M_n[c]
1	**1**	toluene	100	5 000	2.35
2	**1**	$CHCl_3$	97	12 200	2.20
3	**1**	CH_2Cl_2	94	8 300	1.84
4	**1**	THF	15	>1 000	
5	**1**	CCl_4	0		
6	**1**	CH_3OH	0		
7	**2**	toluene	93	25 300	1.64
8	**2**	$CHCl_3$	100	29 400	1.76
9	**2**	CH_2Cl_2	97	43 800	1.72
10	**3**	toluene	93	13 400	2.06
11	**3**	$CHCl_3$	99	12 900	2.27
12	**3**	CH_2Cl_2	87	16 000	2.26

[a] 30 °C, 24 h; [Rh] = 2.0 mM, $[M]_0$ = 0.20 M. [b] Hexane-insoluble product. [c] Determined by GPC (THF eluent, PSt standard).

Polymerization. All the polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock. A typical procedure is as follows: A solution (2.0 mL) of monomer (1.0 mmol) was added to a solution (3.0 mL) of the Rh catalyst (4.0 μmol). The reaction system was kept at 30 °C for 24 h. Polymers formed were isolated by precipitation in a large amount of hexane, filtered, and dried under vacuum to constant weight (yield = 99%; M_n = 20 800, M_w/M_n = 1.47; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.95 (d, 6H, J = 6.3 Hz), 2.06−2.22 (m, 4H), 4.05 (dd, 2H, J = 2.4, 5.4 Hz), 5.65 (s, 1H); cis content: >90%).

Measurements. Monomer conversions were determined by GC (Shimadzu GC-8A; Silicone SE30 (5% on Chromosorb W(AW-DMCS), 80−100 mesh); injection and column temperatures were 200 and 180 °C, respectively) using bromobenzene as an internal standard. The number- and weight-average molecular weights (M_n and M_w, respectively) and polydispersity indices (M_w/M_n) of polymers were measured by GPC at 40 °C with a Jasco PU-980/RI-930 chromatograph; eluent THF, columns KF-805 (Shodex) × 3, molecular range up to 4×10^6, flow rate 1 mL/min, calibrated with polystyrene standards.

Results and Discussion

Polymerization. The polymerization of **1** with a Rh complex (**4**) was studied in various solvents at 30 °C for 24 h (Table 1). The polymerization hardly proceeded in THF and did not proceed at all in carbon tetrachloride or methanol (runs 4−6). The polymerization took place smoothly in toluene, chloroform, and dichloromethane to afford polymers with M_n ranging from 5000 to 12 200 in over 90% yields (runs 1−3). The formed polymer precipitated in 5 min from the reaction mixture when chloroform and dichloromethane were used as polymerization solvents, whereas the polymerization system stayed homogeneous and became highly viscous in toluene solution. Next, the polymerizations of **2** and **3** were examined (runs 7−12). The polymers precipitated in 10 min in dichloromethane, while the polymerization solution became highly viscous in toluene. The polymerizations of **2** and **3** proceeded homogeneously in chloroform to give the polymers with M_n of 29 400 and 12 900 in good yields (runs 8 and 11). The polydispersities of poly(**2**) were smaller than those of poly(**3**), which is probably due to the better solubility of the former polymer.

Proof of the Presence of Long-Lived Active Species. In the case of polymerization of PA catalyzed by Rh, phosphines as additives coordinate to the active species.[15] This suggests that it is possible to control the rate of the present polymerization and further hopefully to induce living polymerization. For the purpose of generating long-lived active species, the polymerization of **2** was carried out in chloroform at 30 °C for 24 h in the presence of various phosphines and triphenyl phosphite. The M_n of the polymers formed in the polymerization employing aromatic phosphines (runs 2−5) decreased compared to those for the polymerizations without any phosphorus additives and with an aliphatic phosphine (run 6) or a phosphite (run 7). This indicates that the polymerization with aromatic phosphines achieves higher initiation efficiencies. No apparent difference was observed among the polymerizations using aromatic phosphines as additives (runs 2−5). In all cases, the addition of various phosphines resulted in the formation of polymers with relatively narrow molecular weight distributions.

Table 2. Effect of Phosphine or Phosphite on the Polymerization of *N*-Propargylamide 2 with Rh Complex 4[a]

		polymer[c]		
run	phosphine or phosphite[b]	yield, %	M_n[d]	M_w/M_n[d]
1	none	100	29 400	1.76
2	$(4\text{-}FC_6H_4)_3P$	100	22 900	1.40
3	Ph_3P	99	20 800	1.47
4	$(4\text{-}CH_3C_6H_4)_3P$	100	21 100	1.41
5	$(4\text{-}CH_3OC_6H_4)_3P$	99	18 700	1.48
6	Bu_3P	98	31 300	1.52
7	$(C_6H_5O)_3P$	95	25 600	1.42

[a] In $CHCl_3$, 30 °C, 24 h; [Rh] = 2.0 mM, $[M]_0$ = 0.20 M. [b] [P]/[Rh] = 1. [c] Hexane-insoluble product. [d] Determined by GPC (THF eluent, PSt standard).

Table 3. Effect of Phosphine/Catalyst Ratio on the Polymerization of *N*-Propargylamide 2 with Rh Complex 4[a]

		polymer[b]		
run	$[Ph_3P]/[Rh]$	yield, %	M_n[c]	M_w/M_n[c]
1	0	100	29 400	1.76
2	1	99	20 800	1.47
3	3	98	21 500	1.43
4	5	100	17 300	1.36
5	10	100	17 800	1.32

[a] In $CHCl_3$, 30 °C, 24 h; [Rh] = 2.0 mM, $[M]_0$ = 0.20 M. [b] Hexane-insoluble product. [c] Determined by GPC (THF eluent, PSt standard).

Ph_3P was chosen as a representative phosphine, and then the effect of phosphine concentration on the polymerization of **2** was examined (Table 3). When the phosphine concentration was increased, the polydispersity became smaller, suggesting that the propagation reaction proceeds more slowly owing to the ligation of the phosphine. When 10 equiv of Ph_3P was added to Rh, the formed polymer exhibited an even smaller polydispersity than with 5 equiv of Ph_3P, but the difference was not significant (runs 4 and 5).

Monomer **2** was completely consumed in 5 min in chloroform at 30 °C in the presence of 5 equiv of Ph_3P to Rh. To monitor the monomer consumption, the polymerization was carried out at 0 °C to decelerate the reaction. The time profile of the polymerization in chloroform at 0 °C is shown in Figure 1. The first-order plot for this time profile displayed a linear relationship, although it somewhat deviated from the origin, which indicates no termination reaction occurred under these conditions. The reason why the line did not pass the origin may be slow initiation.

Under the same conditions, the effect of the ratio of initial monomer concentration to catalyst concentration

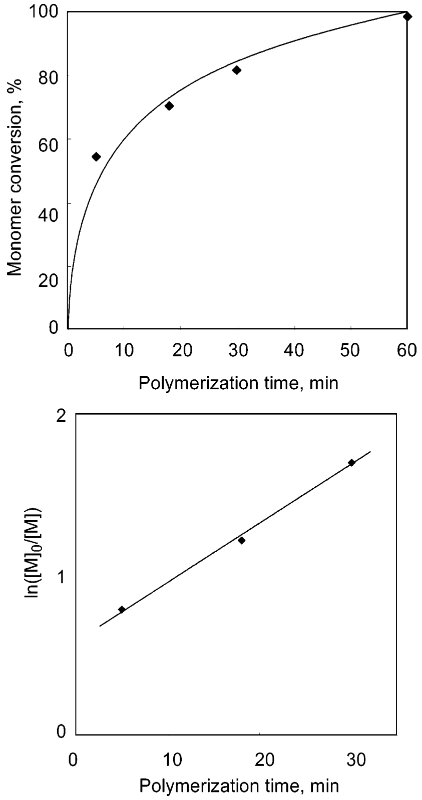

Figure 1. (a, top) Time–conversion curve and (b, bottom) first-order plot of the polymerization of **2** with catalyst **4** (in $CHCl_3$, 0 °C, 1 h; $[M]_0 = 0.20$ M, $[Rh] = 2.0$ mM, $[Ph_3P]/[Rh] = 5$).

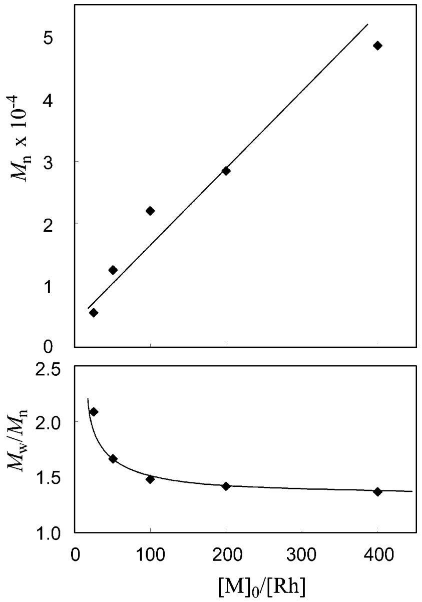

Figure 2. Effect of $[M]_0/[Rh]$ on the M_n and M_w/M_n of the polymer formed in the polymerization of **2** with catalyst **4** (in $CHCl_3$, 0 °C, 1 h; $[M]_0 = 0.20$ M, $[Rh] = 2.0$ mM, $[Ph_3P]/[Rh] = 5$).

($[M]_0/[Rh]$) was studied, where catalyst concentration was kept constant (Figure 2). When the $[M]_0/[Rh]$ was increased, the M_n of polymer increased proportionally, while the M_w/M_n remained almost constant at $[M]_0/[Rh] \geq 100$. We conclude from these results that no chain transfer reaction took place under these conditions. In the case of $[M]_0/[Rh] < 100$, the M_w/M_n was larger, presumably because the ratio of propagation and initiation rates (k_p/k_i) is larger than those of common living polymerizations.

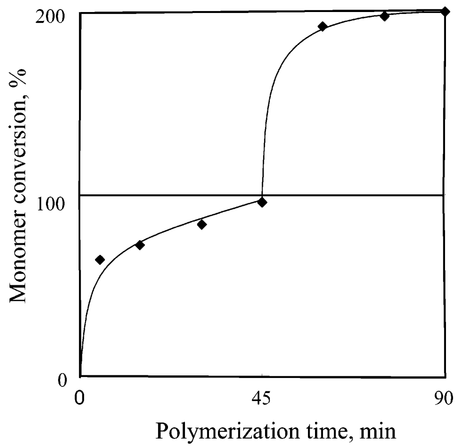

Figure 3. Time–conversion curve for the multistage polymerization of **2** (in $CHCl_3$, 0 °C, 45 min each; $[M]_0 = [M]_{add} = 0.10$ M, $[Rh] = 2.0$ mM, $[Ph_3P]/[Rh] = 5$).

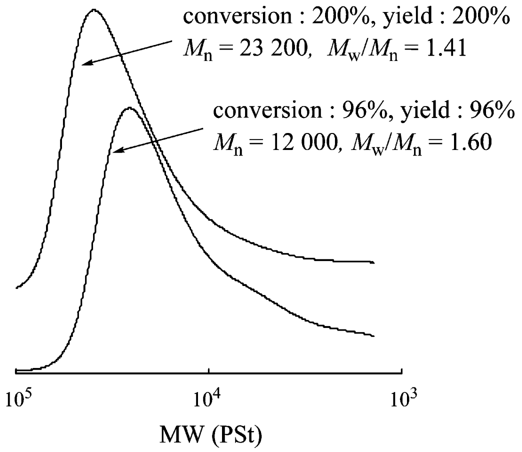

Figure 4. GPC charts of the multistage polymerization of **2** with catalyst **4**: (a) first stage and (b) second stage (in $CHCl_3$, 0 °C, 45 min each; $[M]_0 = [M]_{add} = 0.10$ M, $[Rh] = 2.0$ mM, $[Ph_3P]/[Rh] = 5$).

A multistage polymerization experiment of **2** was attempted (Figures 3 and 4). When monomer was completely consumed (100%), the second monomer feed was supplied to the polymerization system. However, the second monomer feed was not consumed at all. Then, after practically complete consumption of monomer (96%) had been confirmed, the second monomer feed was supplied to the polymerization system. Consequently, the second feed was also consumed completely in due course (Figure 3), and the peak of GPC shifted to a higher molecular weight (MW) region (Figure 4). After the second-stage polymerization, the M_n essentially doubled, while the M_w/M_n remained a relatively small value. Consequently, this polymerization has proceeded via long-lived active species and shows livinglike nature, although the M_w/M_n is somewhat larger than those in common living polymerizations.

Synthesis of Block Copolymer. We next applied this polymerization system to the synthesis of block copolymer by performing the sequential polymerization of **2** and **3** (in $CHCl_3$, 0 °C, 45 min each; $[M]_0 = [M]_{add} = 0.20$ M, $[Rh] = 2.0$ mM, $[Ph_3P]/[Rh] = 5$). Figure 5 shows the GPC charts of the first-stage homopolymer

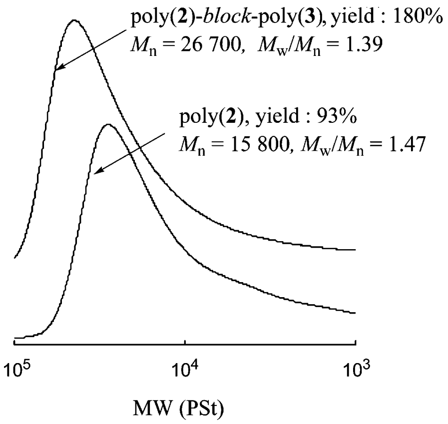

Figure 5. GPC charts of the block copolymerization of 2 and 3: (a) first stage and (b) second stage (in $CHCl_3$, 0 °C, 45 min each; $[M]_0 = [M]_{add} = 0.20$ M, [Rh] = 2.0 mM, $[Ph_3P]/[Rh] = 5$).

and the block copolymer. When the polymerization of **2** was at first carried out, and then monomer **3**, which has a different alkyl chain, was added as the second monomer, the GPC peak of the formed polymer shifted to a higher MW region, keeping the narrow MWD. This means that the block copolymer of **2** and **3** was successfully synthesized. Although the MWD is not very narrow, this is the first example of the synthesis of a block copolymer of *N*-propargylamides.[17]

Conclusion

The living nature was confirmed in the polymerization of *N*-propargylamides catalyzed by the Rh(nbd)(C(Ph)═CPh$_2$)(4-FC$_6$H$_4$)$_3$P/Ph$_3$P system. In this polymerization, the M_w/M_n was around 1.40 and somewhat larger than those in common living polymerizations. This is probably because the k_p/k_i ratio is larger than those in typical living polymerizations. Further, a block copolymer was synthesized from two kinds of *N*-propargylamides.

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(18) The sequential polymerizations of PA and **2** were also examined to prepare the corresponding block copolymers. When PA was employed as the first monomer, the GPC peak became bimodal after addition of **2** as the second monomer. The top of the lower MW peak was the same as that of the first-stage polymer. Eventually the product proved to be a mixture of poly(PA) and poly(**2**) and not the block copolymer. In contrast, when the first monomer was **2**, the GPC of the second-stage product also showed a bimodal distribution, but neither of the peaks agreed with that of the first-stage product. From the data obtained, it is assumed that a mixture of poly(2)-*block*-poly(PA) and homopoly(PA) was formed in this order of monomer addition.

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