Polymer Bulletin 46, 147–152 (2001)

Polymer Bulletin

Polymerization of *N*-substituted 2-propynamides with transition metal catalysts

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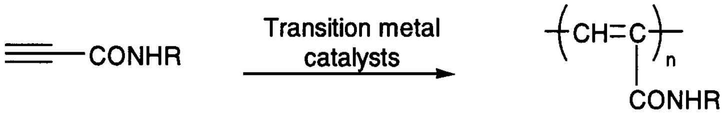
Received: 25 December 2000/Revised version: 17 January 2001/Accepted: 19 January 2001

Summary

Polymerization of *N*-substituted 2-propynamides proceeded in the presence of Pd(II) catalysts such as $[Pd(CH_3CN)_4](BF_4)_2$, $PdCl_2(PhCN)_2$-*n*-BuLi, and $PdCl_2$(nbd)-*n*-BuLi. The molecular weights of the obtained polymers ranged 8,500 to 14,000, depending on the catalysts. From the ^{1}H NMR spectra, these polymers were found to have alternating double bonds in the main chain.

Introduction

Polymers having amide functional groups often exhibit unique properties. For example, the highly hydrophilic character of amide groups contributes to the water-solubility of poly(acrylamides) and poly(oxazolines). Intermolecular hydrogen bonding between the main chains of aromatic poly(amides) also plays an important role for their excellent thermal stability. Thus, introduction of amide linkage onto conjugated polymers such as substituted polyacetylenes would enable the production of new optoelectronic materials. Unfortunately, the polymerization of acetylenes conjugatively connected with amide groups, 2-propynamides, has gathered little attention so far, and only the polymerization of unsubstituted 2-propynamide has been briefly communicated [1]. In this paper, we demonstrate the first example of the polymerization of *N*-substituted 2-propynamide (Scheme 1).



Scheme 1. Polymerization of *N*-substituted 2-propynamide

Experimental

Instruments

^{1}H NMR spectra were recorded on a JEOL EX-400 spectrometer. IR spectra were measured using a Shimadzu FTIR-8100 spectrophotometer. Number- and weight-average molecular weights (M_n, and M_w, respectively) of the polymers were determined by gel permeation chromatography (eluent, THF; three Shodex columns KF805L; polystyrene calibration).

Materials

CH_3CN, toluene, THF, anisole, and dioxane were distilled by the standard procedures. Water was deionized by ion-exchange resin (G-10C, Organo). Commercially available $MoOCl_4$ (Strem), $[(nbd)RhCl]_2$ (Aldrich), $Fe(acetylacetonate)_3$ (Nacalai Tesque), $PdCl_2$ (Nacalai Tesque), $Pd(dba)_2$ (AZmax), $Pd(nbd)Cl_2$ (Aldrich), *n*-BuLi (1.50 mol/L in *n*-hexane, Kanto Chemical), *t*-BuLi (1.54 mol/L in *n*-pentane, Kanto Chemical), MeLi (1.14 mol/L in Et_2O, Kanto Chemical), and Et_2Zn (1.00 mol/L in *n*-hexane, Kanto Chemical) were used without further purification. *n*-Bu_4Sn was purchased from Tokyo Kasei, distilled under reduced pressure from calcium hydride, and stored as toluene solution (200 mmol/L). $WCl_2(CO)_3(AsPh_3)_2$ [2], $(nbd)Rh(H_2O)(tos)$ [3], ReO_3Me [4], $Ni(PPh_3)Cl_2$ [5], $[Pd(CH_3CN)_4]((BF_4)_2$ [6], $Pd(PhCN)_2Cl_2$ [7], $Pd(PPh_3)_2Cl_2$ [8], and $Pd(dppf)Cl_2$ [9] were prepared as described in the literature. *N*-Substituted 2-propynamides were prepared according to the reported method [10].

Procedures

Polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under dry nitrogen. The resulting polymers were isolated by precipitation in a large amount of *n*-hexane and dried under reduced pressure.

Results and Discussion

Polymerization

W and Mo catalysts are effective in the metathesis polymerization of various substituted acetylenes and cycloolefins, while Rh and Fe catalysts induce the insertion polymerization of monosubstituted acetylenes [11], [12]. Polymerization of *N*-*n*-butyl- and *n*-octyl-2-propynamides was first examined by using these traditional Mo, W, Rh, and Fe catalysts (Table I).

No product that precipitated in hexane was obtained in the $MoOCl_4$-*n*-Bu_4Sn and $WCl_2(CO)_3(AsPh_3)_2$ systems. On the other hands, $[(nbd)RhCl]_2$, which polymerizes propiolic esters in acetonitrile [13], provided a hexane-insoluble product as yellow powder. However, GPC and ^1H NMR analyses suggested that the product involved the dimer of *N*-*n*-butyl-2-propynamide. A water-soluble Rh catalyst, $(nbd)Rh(H_2O)(tos)$, which polymerizes acetylenes having polar groups [14], was less effective and produced only low molecular weight oligomers. In a similar way, only a low molecular weight product was obtained with $Fe(acac)_3$-Et_3Al. The ReO_3Me-Et_3Al system, which is known to induce metathesis polymerization of cycloolefins [15], also failed to produce the polymer. Thus, these conventional catalysts were unsuitable for the polymerization of *N*-substituted 2-propynamides.

Gorman et al. have reported that $Ni(PPh_3)_2Cl_2$ and $[Pd(CH_3CN)_4](BF_4)_2$ are effective in the polymerization of *N*-unsubstituted 2-propynamide to yield polymers with M_w of 9,200 and 2,500, respectively [1]. However, only a low molecular weight product with M_w of 1,300 was formed from *N*-*n*-octyl-2-propynamde when $Ni(PPh_3)_2Cl_2$ was employed. In contrast, the polymerization of *N*-*n*-butyl-2-propynamde with $[Pd(CH_3CN)_4](BF_4)_2$ proceeded to give a polymer with M_w of 14,000. Therefore, Pd-based catalysts are likely to promote the polymerization of *N*-substituted 2-propynamides.

Table I. Polymerization of HC≡CCONH–R with Various Transition Metal Catalysts [a]

catalyst	solvent	R	yield (%)[b]	M_n[c]	M_w[c]
$MoOCl_4$–*n*-Bu_4Sn[d]	toluene	*n*-Bu	0	–	–
$WCl_2(CO)_3(AsPh_3)_2$[e]	toluene	*n*-Oct	0	–	–
$[(nbd)RhCl]_2$	CH_3CN	*n*-Bu	55	160	170
$(nbd)Rh(H_2O)(tos)$	H_2O	*n*-Bu	30	1,400	2,600
$Fe(acac)_3$–Et_3Al[f]	toluene	*n*-Oct	16	590	730
ReO_3Me-Et_3Al[g]	toluene	*n*-Bu	8	720	1,100
$NiCl_2(PPh_3)_2$[h]	DMF	*n*-Oct	38	1,100	1,300
$Pd(dba)_2$	toluene	*n*-Bu	50	1,500	1,600
$[Pd(CH_3CN)_4](BF_4)_2$	toluene	*n*-Bu	32	2,700	14,000

[a] at 30 °C, 24 h, $[M]_0 = 0.50$ mol/L, [cat] = 10 mmol/L; [b] *n*-hexane insoluble-products; [c] values measured by GPC (eluent THF) and calibrated with polystyrene standards; [d] $[n\text{-}Bu_4Sn]$ = 10 mmol/L; [e] at 60 °C, [cat] = 4.0 mmol/L; [f] [cat] = $[Et_3Al]$ = 20 mmol/L; [g] $[Et_3Al]$ = 40 mmol/L; [h] at 80 °C.

The polymerization of *N*-butyl-2-propynamide using various Pd-based catalysts was next investigated in order to improve the yield as well as molecular weight of the polymer (Table II). When $Pd(PhCN)_2Cl_2$ was used in the absence of any cocatalyst, a hexane-insoluble product was obtained in high yield, but this product only had a low molecular weight. In contrast, $Pd(PhCN)_2Cl_2$ combined with *n*-BuLi was effective to yield a polymer with M_w of 11,000. A relatively high molecular weight polymer (M_w = 8,500) was also obtained with $Pd(nbd)Cl_2$-*n*-BuLi. $Pd(PPh_3)_2Cl_2$-*n*-BuLi and $Pd(dppf)Cl_2$-MeLi systems produced only low molecular weight products in low yields. Strongly ligating phosphine ligands appeared to reduce the catalytic activities.

Table II. Polymerization of HC≡CCONH–*n*-Bu with Various Pd(II)-Based Catalysts [a]

catalyst	yield (%)[b]	M_n[c]	M_w[c]
$PdCl_2(PhCN)_2$	100	1,300	1,800
$PdCl_2(PhCN)_2$–*n*-BuLi	73	2,400	11,000
$PdCl_2(nbd)$–*n*-BuLi	63	2,500	8,500
$PdCl_2(PPh_3)_2$–*n*-BuLi	27	1,100	1,600
$PdCl_2(dppf)$–MeLi	35	1,400	1,600

[a] in toluene, 30 °C for 24 h, $[M]_0 = 0.50$ mol/L, [Pd] = [cocatalyst] = 10 mmol/L; [b] *n*-hexane insoluble-products; [c] values measured by GPC (eluent THF) and calibrated with polystyrene standards.

The conditions for the $Pd(PhCN)_2Cl_2$-*n*-BuLi catalyzed polymerization were further optimized by changing the alkyl metal cocatalyst (Table III). When *t*-BuLi, MeLi, and *n*-Bu_4Sn were employed, the yields of the products increased but the molecular weights decreased in comparison with the system with *n*-BuLi. The yields and molecular weights of the products were also unsatisfactory in the cases of Et_2Zn and Et_3Al. Thus, *n*-BuLi is the most suitable cocatalyst for the $Pd(PhCN)_2Cl_2$ system.

Table III. Effect of Cocatalysts on the Polymerization of HC≡CCONH–*n*-Bu with $PdCl_2(PhCN)_2$[a]

cocatalyst	yield (%)[b]	M_n[c]	M_w[c]
none	100	1,300	1,800
n-BuLi	73	2,400	11,000
t-BuLi	100	1,400	1,900
MeLi	72	1,600	2,000
n-Bu_4Sn	94	1,200	1,600
Et_2Zn	17	900	1,000
Et_3Al	14	800	970

[a] in toluene, 30 °C, 24 h, $[M]_0 = 0.50$ mol/L, [cat] = [cocatalyst] = 10 mmol/L; [b] *n*-hexane insoluble-products; [c] values measured by GPC (eluent THF) and calibrated with polystyrene standards.

Table IV shows the effects of solvents. The polymerizations in polar solvents such as anisole and dioxane provided low yields of low molecular weight oligomers. In THF, a high molecular weight polymer was obtained. However, the ^1H NMR spectrum indicated that the main chain of this polymer contained the unit formed by the hydrogen migration polymerization (see below). This is because the base-catalyzed hydrogen migration polymerization of *N*-substituted 2-propynamide readily proceeds in polar solvents [16]. Thus, less polar solvents such as toluene are suitable as solvents.

Table IV. Effect of Solvents on the Polymerization of HC≡CCONH–*n*-Bu with $Pd(PhCN)_2Cl_2$–*n*-BuLi[a]

solvent	yield (%)[b]	M_n[c]	M_w[c]
Toluene	73	2,400	11,000
Anisole	23	780	900
Dioxane	49	1,000	1,200
THF	30	5,700	11,000

[a] at 30 °C, 24 h, $[M]_0 = 0.50$ mol/L, [cat] = [*n*-BuLi] = 10 mmol/L; [b] *n*-hexane insoluble-products; [c] values measured by GPC (eluent THF) and calibrated with polystyrene standards.

Finally, the effect of the concentration of *n*-BuLi was investigated (Table V). When the concentration of *n*-BuLi was more or less than that of the Pd catalyst, only low molecular weight products were obtained. The reaction of palladium salts with alkyllithiums generally gives the corresponding alkylpalladiums. When the formed alkylpalladiums possess a ß-hydrogen, they are unstable and readily decompose to give palladium hydride complexes. Therefore, the palladium hydride formed in situ is likely to contribute to the initiation.

Table V. Effect of the Concentration of *n*-BuLi on the Polymerization of HC≡CCONH–*n*-Bu with $Pd(PhCN)_2Cl_2$–*n*-BuLi[a]

[*n*-BuLi] / [Pd]	yield (%)[b]	M_n[c]	M_w[c]
0	100	1,300	1,800
0.25	100	1,200	1,800
1	73	2,400	11,000
2	75	1,200	1,500
4	45	1,600	3,900

[a] in toluene, 30 °C, 24 h, $[M]_0$ = 0.50 mol/L, [Pd] = 10 mmol/L; [b] *n*-hexane insoluble-products; [c] values measured by GPC (eluent THF) and calibrated with polystyrene standards.

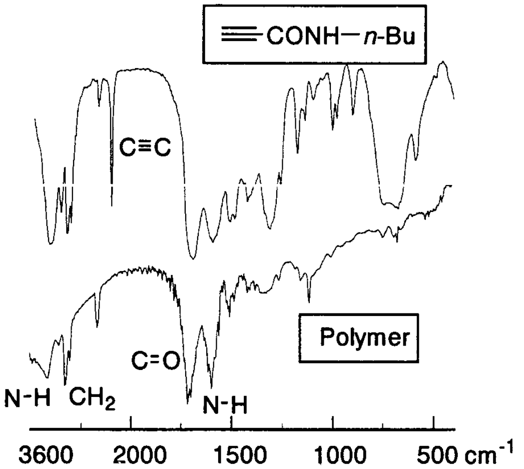


Figure 1. IR spectra of monomer and poly(HC≡CCONH–*n*-Bu) prepared with $Pd(PhCN)_2Cl_2$–*n*-BuLi.

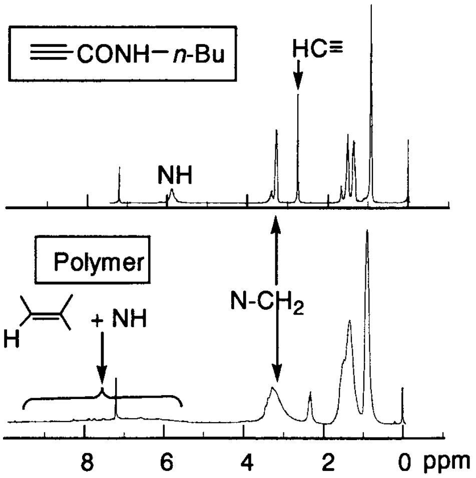


Figure 2. ^1H NMR spectra of monomer and poly(HC≡CCONH–*n*-Bu) prepared with $Pd(PhCN)_2Cl_2$–*n*-BuLi (measured in $CDCl_3$).

Characterization

Figures 1 and 2 show IR and ^1H NMR spectra of *N*-*n*-butyl-2-propynamide and poly(*N*-*n*-butyl-2-propynamide) prepared with $Pd(PhCN)_2Cl_2$-*n*-BuLi. The IR spectrum of *N*-*n*-butyl-2-propynamide exhibited the stretching vibration of C≡C at 2108cm^{-1}. This peak completely vanished after the polymerization. Similarly, ^1H NMR indicated that the peak due to the acetylenic proton in the monomer was not observed in the spectrum of the polymer. Thus, the triple bond of the monomer was completely consumed upon the polymerization. If the polymerization of *N*-substituted 2-propynamides proceeds through the hydrogen migration process, the resultant polymers contain secondary amide repeating units, -CH=CH-CO-NR-, in the main chain [16]. In the IR spectrum of the present polymer from *N*-*n*-butyl-2-propynamide, the absorptions of the deformation and stretch vibrations N-H band were detected at 1541 cm^{-1} and 3400 cm^{-1}. respectively. The ^1H NMR spectrum did not display the peaks at around 5.8 and 8.3 ppm which are assigned to the -CH=CH- double bonds formed by the hydrogen migration process. In contrast, a very broad peak was seen in the region of 5-8 ppm in the present polymers. This is a typical phenomenon for substituted polyacetylenes with less controlled stereoregularity. Therefore, the main chain skeleton of this polymer should be the alternating double bonds.

References

1. Gorman CB, Vest RW, Palovich TU, Serron S (1999) Polym Mater Sci Eng 80:451
2. Colton R, Tomkins IB (1966) Aust J Chem 21:1143
3. Kölle U, Görissen R, Wagner T (1995) Chem Ber 128:911
4. Herrmann WA, Kuchler JG, Weichselbaumer G, Herdtweck E, Kiprof P (1989) J Organomet Chem 372:351
5. Booth G, Chatt J (1965) J Chem Soc 3239
6. Lai TW, Sen A (1984) Organometallics 3:866
7. Doyle JR, Slade PE, Jonassen HB (1960) Inorg Synth 6:218
8. Chatt J, Mann FG (1939) J Chem Soc 1622
9. Hayashi T, Konishi M, Kumada M (1979) Tetrahedron Lett 1871
10. Coppola GM, Damon RE (1993) Synth Commun 23:2003
11. Masuda T (1997) Catalysis in Precision Polymerization. Kobayashi S (ed) Wiley, Chichester (Chapter 2.4)
12. Masuda T (1996) Polymeric Material Encyclopedia Vol. 1. Salamone JC (ed) CRC, New York (p 32)
13. Nakako H, Nomura R, Tabata M, Masuda T (1999) Macromolecules 32:2861
14. Goto H, Saito MA, Onouchi H, Maeda K, Yashima E (2000) Polym Prep Japan 49:7:1371
15. Herrmann WA, Wagner W (1991) Angew Chem Int Ed Engl 30:1636
16. Nomura R, Nakako H, Masuda T (2000) Polym J 32:303