SHORT COMMUNICATION

N-Substituted-2-propynamides. Highly Reactive Acetylene Derivatives toward Hydrogen Migration Polymerization

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Hydrogen migration polymerization is one of the unique methodologies for the preparation of functional materials due to its ability to provide polyamides from vinyl monomers. Since the discovery of hydrogen migration polymerization of acrylamide by Breslow *et al.*,[1] several vinyl monomers including *N*-substituted acrylamides, methacrylamides, vinylbenzamides and acrylic acid have proven to polymerize in this fashion.[2] However, previous studies on hydrogen migration polymerization are limited to those for only vinyl monomers, and no example has been demonstrated for the hydrogen migration polymerization of acetylenic monomers, notwithstanding the excellent electrophilicity and low thermal and ionic polymerizability of electron-deficient acetylenes. In the course of our systematic research on the chemistry of acetylene polymerization,[3] we recently recognized very high reactivity of *N*-substituted-2-propynamides toward hydrogen migration polymerization. Here, we wish to report the first example for the hydrogen migration polymerization of electron-deficient acetylene, *N*-substituted 2-propynamides (Scheme 1).

EXPERIMENTAL

GPC analyses were carried out using two Shodex KF 805 L columns (eluent, tetrahydrofuran (THF) after calibration with standard polystyrene. Melting points were measured with a Yanaco micro melting point apparatus. IR spectra and NMR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer and a JEOL EX-270 or EX-400 spectrometer, respectively. Gas chromatographic analyses were performed by using a Shimadzu Model GC-8 A chromatograph. Acetonitrile and toluene were dried over CaH_2 and distilled under nitrogen. *N*, *N*-Dimethylformamide (DMF) and dimethyl sulfoxide (DM

SO) were dried over CaH_2 and distilled under reduced pressure. Dioxane was dried over sodium, which was followed by the distillation under nitrogen. The solvents used in the preparation of the monomers were used without purification. The monomers were prepared according to the reported manner.[4] The spectral and analytical data of **1** are as follows. Mp 33—36℃. ^{1}H NMR ($CDCl_3$) δ 0.88 (t, CH_3, $J = 6.8$ Hz), 1.20—1.60 (m, CH_2), 2.76 (s, HC≡C), 3.28 (q, NHCH_2, $J = 4.6$ Hz), 6.18 (brs, NH) ; ^{13}C NMR ($CDCl_3$) δ 14.00, 22.54, 26.75, 29.10, 31.68, 39.88, 72.87, 77.40, 152.13 ; IR 3308, 2928, 2110, 1639, 1545, 1277 cm^{-1}. *Anal.* Calcd for $C_{11}H_{19}NO$: C, 72.88 ; H, 10.56 ; N, 7.73. Found : C, 72.64 ; H, 10.54 ; N, 7.68.

Polymerizations were carried out by the addition of the monomer solution in acetonitrile into the suspension of an initiator in acetonitrile. After the polymerization, the precipitated product was dissolved in $CHCl_3$, and the organic phase was washed with water, dried over Na_2SO_4, and concentrated to give the polymer. Further purification was performed by the reprecipitation into hexane.

RESULTS AND DISCUSSION

In order to optimize the polymerization conditions, *N*-*n*-octyl-2-propynamide (**1**)[4] was employed as a monomer based on the prospect that the stiffness of the main chain structure would reduce the solubility of the polymer. Polymerizations of **1** were conducted by using conventional anionic initiators, and the results are summarized in Table I. The use of polar solvents resulted in the polymers in good yields (runs 4, 5), while polymerizations in less polar solvents such as toluene and dioxane gave no polymer (runs 1, 2). It should be noted that the present polymerization proceeds under extremely mild conditions to give polymers with relatively high molecular weights. Namely, a decrease in the polymerization temperature from 80℃ increased both the yield and molecular weight of poly(**1**) (runs 5—9), and maximum values were obtained at around 0—30℃(runs 7, 8). This is in contrast to the traditional hydrogen migration polymerizations of vinyl monomers, where very severe conditions are generally required.[2] The extent of hydrogen mi-
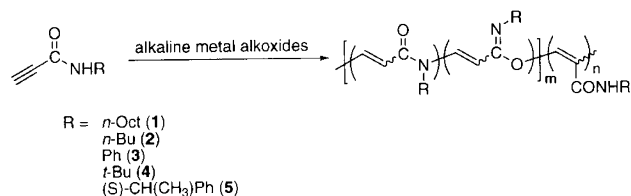
$$R = \text{n-Oct (1)}$$
n-Bu (2)
Ph (3)
t-Bu (4)
(S)-CH(CH₃)Ph (5)

Scheme 1.

Table I. Polymerization of **1** with alkaline metal alkoxides[a]

Run	Solvent	Initiator	$\dfrac{\text{Temp}}{°C}$	$\dfrac{\text{Conv.}^{b}}{\%}$	$\dfrac{\text{Yield}^{c}}{\%}$	M_n^{d}	M_w/M_n^{d}	m/n^{e}
1	Toluene	t-BuOK	80	37	0	—	—	—
2	Dioxane	t-BuOK	80	12	0	—	—	—
3	DMF	t-BuOK	80	44	7	6400	1.99	ND[f]
4	DMSO	t-BuOK	80	100	67	1900	3.05	44/56
5	CH₃CN	t-BuOK	80	70	70	4800	2.76	45/55
6	CH₃CN	t-BuOK	60	78	73	7200	2.14	55/45
7	CH₃CN	t-BuOK	30	100	70	10000	1.99	61/39
8	CH₃CN	t-BuOK	0	100	78	9500	2.58	59/41
9	CH₃CN	t-BuOK	−30	40	33	8100	2.07	75/25
10	CH₃CN	t-BuOLi	30	38	ND[f]	6800	2.72	99/1
11	CH₃CN	MeONa	30	53	ND[f]	9700	2.51	90/10
12	CH₃CN	PhOCs	30	100	100	4900	1.30	70/30

[a] Conditions ; $[1]_0 = 500$ mM, 24 h, 1/Cat$=25/1$ [b] Determined by GC.   [c] Hexane-insoluble part.   [d] Estimated by GPC (THF, PSt standard).   [e] Determined by ¹H NMR.   [f] Not determined.
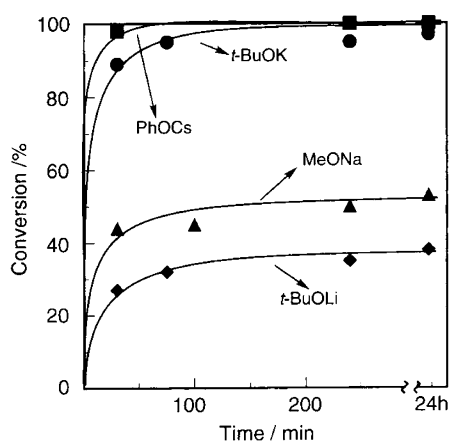

Figure 1. Time-conversion curves for the polymerization of **1** with various initiators ($[1]_0=1.0$ M, 1/Cat$=50$, 30℃, in acetonitrile).

Figure 2. ¹H NMR spectrum of poly(**1**) in CDCl₃ (run 7 in Table I).

gration also increased as the temperature was lowered, and the hydrogen migration polymerization dominates over the acetylene-polymerization at reduced temperature.

Countercations remarkably influenced the polymerization behavior (runs 7 and 10—12). It is worth noting that, when t-BuOLi was used, almost complete selectivity of hydrogen migration process was obtained (run 10). This contrasts with the fact that the addition of inhibitors is indispensable to achieve selective hydrogen migration polymerization of vinyl monomers. By comparison of the polymerizations with metal alkoxides (runs 7, 10, and 11), the selectivity of hydrogen migration process was found to increase in the order of K<Na<Li, which agrees well with the nucleophilicity of alkaline metal alkoxides.

Very high polymerizability of N-substituted-2-propynamides can be recognized not only by the fact that polymerization proceeds under mild conditions but also by the high polymerization rate. Time-conversion curves of the polymerization of **1** (Figure 1) clearly show very rapid consumption of **1** in the presence of t-BuOK or PhOCs even at 30℃. At elevated temperature (80℃), polymerization was instantaneously completed leading to immediate precipitation of polymer just after the addition of **1**. Copolymerization of **1** with acrylamide also supports the high reactivity of propynamides. Namely,
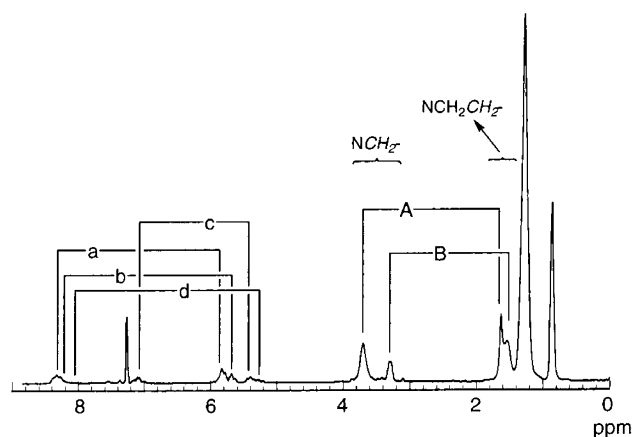
treatment of the acetonitrile solution containing **1** and acrylamide (1 : 1) with t-BuOK at 60℃ for 2 h resulted in the selective formation of poly(**1**), while no consumption of acrylamide was detected.

Long alkyl pendant groups are necessary for the formation of soluble polymers due to the stiffness of the main chain. For example, polymers almost completely soluble in chloroform were obtained from N-butyl-2-propynamide (**2**) in 52 and 61% yields with t-BuOK and MeONa, respectively. The molecular weight of the chloroform-soluble part of poly(**2**) was 2700—3000 (GPC). However, substitution of the alkyl group on nitrogen by a phenyl ring led to a polymer (68—80%) with poor solubility in chloroform. Bulky substituents seem to retard the polymerization because no polymer was obtained from N-t-butyl (**4**) and N-(S)-phenethyl-2-propynamide (**5**) under the present conditions.

Characterization of poly(**1**) was carried out by IR and ¹H NMR spectroscopies. The IR spectrum of **1** shows characteristic absorptions attributed to N–H (3320 and 3460 cm⁻¹) and C=O stretching (1639 cm⁻¹) of the amide group. The former was not clearly observed in the spectrum of poly(**1**), which reveals the absence or very low content of N–H bond in the polymer. The presence of disubstituted vinyl groups was also readily recognized in the ¹H NMR spectrum (Figure 2). It should be noted that almost identical ¹H NMR spectrum was obtained when
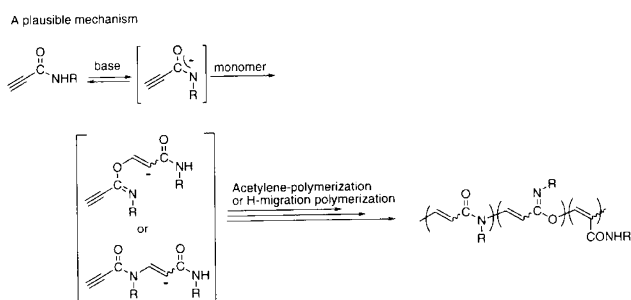
Sheme 2.

the polymerization was carried out in the presence of a large excess of t-butyl alcohol. All these data suggest that the polymerization mechanism involves the hydrogen migration process.[5]

However, the region of vinyl protons (δ 5.0—8.5) is relatively complicated, implying that the polymer has plural main-chain structures. The ^{1}H–^{1}H COSY spectrum of poly(1) clearly indicated the presence of four kinds of vinyl groups as shown in Figure 2 (a—d). The signals due to the methylene protons attached to nitrogen were also observed at 3.3 and 3.7 ppm. These methylene signals correlate to those at 1.5 and 1.6 ppm, respectively, as denoted by arrows A and B. Coupling constants of the vinyl protons were calculated to be 10—15 Hz by using several well-resolved peaks, which means that both cis and trans double bonds exist in the main chain. It is unreasonable to assume that the presence of both geometrical structures yields the large difference in the chemical shift between two kinds of methylene signals (A and B). Considering the fact that the base-promoted alkylation of carboxylic amides with alkyl halides at times competes with O-alkylation, the polymerization mechanism may involve 1,4-addition by O-anion to give the imino ester structure. The presence of the imino ester structure was also indicated by the presence of a very intense absorption at 1586 cm^{-1} in the IR spectrum of poly(1). This absorption band was obviously stronger

than that due to the C=O stretching (1662 cm^{-1}) of the amide groups in the main chain. This excludes the possibility that the absorption at 1586 cm^{-1} originates from the bending vibration of N–H since the bending vibration of N–H is generally weaker than the stretching vibration of C=O group. Therefore, an explanation of the absorbance at 1586 cm^{-1} can be given by the presence of the imino ester group in the polymer backbone. These results give a plausible polymerization mechanism as illustrated in Scheme 2.

In summary, we have demonstrated the first example of the hydrogen migration polymerization of substituted acetylenes. The present system is potentially useful because alternating copolymers of acetylene with isocyanates are formally accessible. Investigation of polymerization conditions to control the polymer structure is currently undergoing.

REFERENCES AND NOTES

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3. For reviews of polymerization of substituted acetylenes, see (a) T. Masuda, "Catalysis in Precision Polymerization," S. Kobayashi, Ed., Wiley, Chichester, 1997, Chapter 2.4. (b) T. Masuda, "Polymeric Material Encyclopedia," J. C. Salamone, Ed., Vol. 1, CRC, New York, N.Y., 1996, pp 32—39.
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5. The vinyl protons of monosubstituted polyacetylenes are usually very broad and at times undetectable unless the polymer backbone has very high cis stereoregularity. Therefore, we believe that vinyl protons generated by the acetylene polymerization are not clearly detected. Therefore, it seems appropriate to estimate the ratio of hydrogen migration unit to acetylene polymerization unit from the integrated intensities of the vinyl (a—d) and methylene protons (A and B).