

## Synthesis of Poly(propargyl esters) with Rhodium Catalysts and Their Characterization

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### Summary

Propargyl esters ( $\text{HC}\equiv\text{CCH}_2\text{OC}(=\text{O})\text{R}$ ; **1**:  $\text{R} = n\text{-C}_5\text{H}_{11}$ , **2**:  $\text{R} = \text{CH}_3$ , **3**:  $\text{R} = \text{CHBrCH}_3$ , **4**:  $\text{R} = \text{C}_6\text{H}_5$ , **5**:  $\text{R} = \text{C}(\text{C}_6\text{H}_5)_3$ ) were polymerized by using  $(\text{nbd})\text{Rh}^+(\eta^6\text{-Ph-B}^-\text{Ph}_3)$  ( $\text{nbd} = 2,5\text{-norbornadiene}$ ) to produce poly(**1**)–poly(**5**) with molecular weights in the range of  $M_n = 4,900\text{--}40,000$ . Poly(**1**), poly(**3**) and poly(**4**) were readily soluble in common organic solvents such as toluene, THF and  $\text{CHCl}_3$ , and poly(**2**) showed similar solubility behavior except that it was insoluble in THF. Poly(**5**) did not dissolve in any organic solvent. Poly(**1**) was yellow oil, while poly(**2**)–poly(**5**) were yellow solids. Poly(**1**)–poly(**4**) exhibited UV-vis absorptions in a range of 300–425 nm, which are attributed to the conjugation of the main chain. All the polymers were thermally stable up to 150–200 °C.

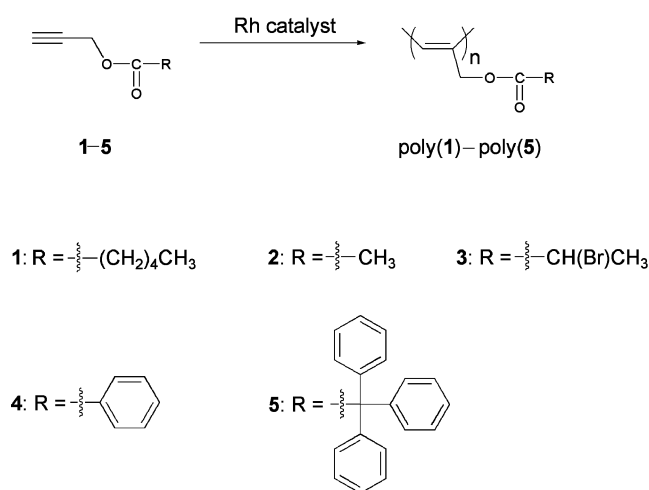
### Introduction

Substituted polyacetylenes are well-known conjugated polymers, which display unique properties such as semiconductivity, high gas permeability, helix formation, and nonlinear optical properties [1,2]. Among a rich variety of these polymers, poly(propargyl esters) are a class of monosubstituted polyacetylenes, which show potential as humidity-sensitive materials [3–5]. The polymerization of propargyl esters was mainly carried out by Pd, Mo and W transition metal catalysts [3–8]. For example, propargyl acetate (**2**) and propargyl benzoate (**4**) were polymerized by using a Pd acetylidyde catalyst,  $\text{Pd}(\text{PPh}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2$ , yielding soluble polymers with high molecular weights ( $M_n = 15,000\text{--}21,000$ ) in good yields (71–80%) [7].

Since rhodium complexes are effective for the polymerization of monosubstituted acetylenes carrying polar functional groups, they are expected to catalyze the polymerization of propargyl esters as well. However, only a few propargyl esters bearing chiral pendant groups were polymerized by a zwitterionic Rh catalyst,  $(\text{nbd})\text{Rh}^+(\eta^6\text{-Ph-B}^-\text{Ph}_3)$ , to obtain helical polyacetylenes [9,10]. To the best of our knowledge, the polymerization of propargyl esters by Rh catalysts has not been investigated in details except that the polymerization of propargyl hexanoate (**1**) catalyzed by  $(\text{nbd})\text{Rh}^+(\eta^6\text{-Ph-B}^-\text{Ph}_3)$  was briefly communicated [9]. Thus it is

interesting to examine the polymerization behavior of propargyl esters having aliphatic or aromatic groups by using Rh catalysts and to study the polymer properties.

This paper reports on the polymerization of propargyl esters (**1–5**) with Rh catalysts (Scheme 1). The effects of monomer concentration, polymerization temperature and solvents were examined in the polymerization of **1–5**. The resulting polymers were characterized by  $^1\text{H}$  NMR, IR and UV-vis, and their thermal stability was examined by TGA.



**Scheme 1.** Polymerization of monomers **1–5**.

## Experimental

### Measurements

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in chloroform-*d* on a JEOL EX-400 spectrometer. Infrared spectra (IR) were measured using a JASCO FTIR-4100 spectrophotometer. The number- and weight-average molecular weights ( $M_n$  and  $M_w$ , respectively) of polymers were determined by gel permeation chromatography (GPC) on a Jasco Gulliver System (PU-980, CO-965, RI-930, and UV-1570) equipped with polystyrene gel columns (Shodex K804, K805, and J806), using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min, calibrated by polystyrene standards at 40 °C. UV-vis spectra were measured on a Shimadzu UV-2200 spectrophotometer. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA thermal analyzer.

### Materials

$\text{WCl}_6$  (Aldrich),  $\text{MoCl}_5$  (Aldrich),  $\text{Ph}_4\text{Sn}$  (TCI), and triethylamine ( $\text{Et}_3\text{N}$ ) (Wako) were purchased and used without further purification. Monomers **2** (Wako) and **4** (Aldrich) were used after distillation under reduced pressure. Monomer **3** [11],  $[(\text{nb})\text{RhCl}]_2$  (nbd = 2,5-norbornadiene) [12] and  $(\text{nbd})\text{Rh}^+(\eta^6\text{-Ph-B}^-\text{Ph}_3)$  [13] were synthesized according to the literature. Tetrabutyltin (*n*- $\text{Bu}_4\text{Sn}$ ) and all the solvents for polymerization and monomer synthesis were purified by the standard methods. The

reagents for monomer synthesis were commercially obtained and used without purification.

#### *Synthesis of Propargyl Hexanoate (1)*

Monomer **1** was synthesized according to the literature method [14]: Hexanoic acid (5.67 g, 48.9 mmol), 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) (10.3 g, 53.7 mmol), 4-(dimethylamino)pyridine (DMAP) (0.672 g, 6.0 mmol), and propargyl alcohol (3.03 g, 53.7 mmol) in 90 mL of dry CH<sub>2</sub>Cl<sub>2</sub> were stirred overnight. The mixture was filtered, and the filtrate was evaporated. The resulting oil was purified by silica gel column chromatography eluted with hexane to give colorless liquid in 72% yield. <sup>1</sup>H NMR (ppm): 0.90 (t, *J* = 6.40 Hz, -CH<sub>3</sub>, 3H), 1.33 (m, -(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>, 4H), 1.64 (m, -CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>, 2H), 2.33 (t, *J* = 7.20 Hz, O<sub>2</sub>C-CH<sub>2</sub>-CH<sub>2</sub>, 2H), 2.51 (s, H-C≡C, 1H), 4.69 (s, HC≡C-CH<sub>2</sub>-, 2H). <sup>13</sup>C NMR (ppm): 13.71, 22.13, 24.34, 31.06, 33.77, 51.57, 74.59, 76.68, 172.76. IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 3294, 2958, 2933, 2130, 1743. Anal. Calcd for C<sub>9</sub>H<sub>14</sub>O<sub>2</sub> (154.2): C, 70.10; H, 9.15. Found: C, 70.07; H, 9.15.

#### *Synthesis of Propargyl Triphenylacetate (5)*

This compound was prepared following a procedure similar to that of monomer **1** by reacting triphenylacetic acid (4.69 g, 16.3 mmol) with propargyl alcohol (1.01 g, 17.9 mmol). Purification of the crude product was carried out by silica gel column chromatography eluted with hexane/ethyl acetate = 10/1 (volume ratio) to give a white solid in 83% yield. Melting point: 123–124 °C. <sup>1</sup>H NMR (ppm): 2.39 (s, H-C≡C, 1H), 4.74 (s, -CH<sub>2</sub>-, 2H), 7.14–7.26 (m, aromatic H, 15H). <sup>13</sup>C NMR (ppm): 52.74, 67.16, 75.09, 77.14, 126.92, 127.65, 130.16, 142.39, 172.73. IR (KBr, cm<sup>-1</sup>): 3270, 2126, 1808, 1735. Anal. Calcd for C<sub>23</sub>H<sub>18</sub>O<sub>2</sub> (326.4): C, 84.64; H, 5.56. Found: C, 84.80; H, 5.51.

#### *Polymerization*

Polymerizations were carried out under an argon atmosphere in a Schlenk tube equipped with a three-way stopcock. A typical procedure is as follows: The monomer solution was prepared in a Schlenk tube by mixing a monomer and a solvent under the conditions described in footnotes of Tables. Another Schlenk tube was charged with a main catalyst, a cocatalyst, and the solvent. The catalyst solution was aged at 60 °C (for Mo and W catalysts) for 10 min. In the case of Rh catalysts, the catalyst solution was used without the aging process. Then the monomer solution was added to the catalyst solution, and polymerization was carried out for a given time at a given temperature. Polymer was precipitated in a large amount of methanol, filtered, and dried in vacuum overnight. The yield of the polymer was determined by gravimetry.

#### *Spectroscopic Data of the Polymers*

In the following <sup>1</sup>H NMR data, all peaks except for those with descriptions have broad singlet shape.

Poly(**1**) IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 2967, 2932, 2871, 1738, 1164, 993. <sup>1</sup>H NMR (ppm): 0.86 (-CH<sub>3</sub>, 3H), 1.27 (-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>, 4H), 1.56 (-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>, 2H), 2.27 (O<sub>2</sub>C-CH<sub>2</sub>-CH<sub>2</sub>, 2H), 4.69 (-HC=C-CH<sub>2</sub>-, 2H), 6.25 (-HC=C-, 1H). Poly(**2**) IR (KBr, cm<sup>-1</sup>):

2942, 1737, 1375, 1233, 1028, 604.  $^1\text{H}$  NMR (ppm): 2.03 ( $-\text{CH}_3$ , 3H), 4.59 ( $-\text{HC}=\text{C}-\text{CH}_2-$ , 2H), 6.26 ( $-\text{HC}=\text{C}-$ , 1H). Poly(**3**) IR (KBr,  $\text{cm}^{-1}$ ): 2981, 2931, 1735, 1218, 1154.  $^1\text{H}$  NMR (ppm): 1.81 (br d,  $-\text{CH}_3$ , 3H), 4.43 (br q,  $-\text{CHBr}-$ , 1H), 4.81 ( $-\text{HC}=\text{C}-\text{CH}_2-$ , 2H), 6.41 ( $-\text{HC}=\text{C}-$ , 1H). Poly(**4**) IR (KBr,  $\text{cm}^{-1}$ ): 3062, 2946, 1720, 1268, 1108, 708, 686.  $^1\text{H}$  NMR (ppm): 4.78 ( $-\text{HC}=\text{C}-\text{CH}_2-$ , 2H), 6.44 ( $-\text{HC}=\text{C}-$ , 1H), 7.12–8.10 (br m, aromatic H, 5H). Poly(**5**) IR (KBr,  $\text{cm}^{-1}$ ): 3057, 3022, 1731, 1492, 1446, 1170, 699. Due to poor solubility,  $^1\text{H}$  NMR of poly(**5**) was not measured.

## Results and discussion

### Polymerization

Table 1 lists the results of the polymerization of **1** by using Mo, W and Rh catalysts. Group 6 transition metal chlorides,  $\text{WCl}_6$  and  $\text{MoCl}_5$ , in combination with alkylating agents ( $\text{Ph}_4\text{Sn}$  and  $n\text{-Bu}_4\text{Sn}$ ) serve as active catalysts in the metathesis polymerization of relatively polar monosubstituted acetylenes [15]. Thus,  $\text{WCl}_6/\text{Ph}_4\text{Sn}$  and  $\text{MoCl}_5/n\text{-Bu}_4\text{Sn}$  were used as catalysts to polymerize monomer **1** in toluene at  $30\text{ }^\circ\text{C}$ , but no polymeric products were obtained even after 24 h. Polymerization did not take place in dioxane, either, even at a higher temperature of  $60\text{ }^\circ\text{C}$ . These results are possibly due to the poisoning interactions of the ester group with the transition metal compounds. In contrast, a frequently used catalyst for the polymerization of polar monosubstituted acetylenes,  $[(\text{nb})\text{RhCl}]/\text{Et}_3\text{N}$ , resulted in the formation of a polymer with a number-average molecular weight ( $M_n$ ) of 20,000 in 64% yield (Run 4). Under the same conditions,  $(\text{nb})\text{Rh}^+(\eta^6\text{-Ph-B}^-\text{Ph}_3)$  also afforded a polymer in a similar way (Run 6). The highest polymer yield (77%) was accomplished when polymerization was conducted at a monomer concentration of 2.0 M, where the  $M_n$  of polymer was 17,000 (Run 7). The polymerization at  $0\text{ }^\circ\text{C}$  gave a high molecular weight ( $M_n = 40,000$ ) polymer in a moderate yield (50%), whereas the polymer formed at  $80\text{ }^\circ\text{C}$  possessed a rather low molecular weight ( $M_n = 9,100$ ) (Run 8, 9). This is possibly due to the instability of the active species and/or chain termination reactions at high temperature. Further increment of the monomer concentration to 3.0 M significantly decreased the  $M_n$  from 17,000 to 4,900 (Run 10).

Table 2 shows the result of solvent effects on the polymerization of **1** with  $(\text{nb})\text{Rh}^+(\eta^6\text{-Ph-B}^-\text{Ph}_3)$  at  $30\text{ }^\circ\text{C}$ . THF was a favorable polymerization solvent with respect to both polymer yield and molecular weight. Toluene,  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  also worked as useful polymerization solvents, although polymer yield as well as molecular weight more or less decreased. In contrast, anisole and dioxane were not suitable solvents because the molecular weights of polymers were low with broad molecular weight distributions. The use of dimethyl sulfoxide (DMSO) and  $N,N$ -dimethylformamide (DMF) as polymerization solvents produced poly(**1**)s with high molecular weights ( $M_n = 21,000\text{--}23,000$ ) in high yields (79–91%), although the molecular weight distributions were rather broad ( $M_w/M_n = 5.4\text{--}8.2$ ). On the other hand, the polymerization did not proceed in  $\text{CH}_3\text{CN}$ .

The polymerization of monomers **2–5** was examined by using the zwitterionic catalyst in THF (Table 3). In all cases, polymers were obtained in moderate yields (55–62%).

Table 1. Polymerization of **1**<sup>a</sup>

Run	Catalyst	Solvent	Temp (°C)	Time (h)	[M] <sub>0</sub> (mol/L)	Polymer <sup>b</sup>		
						Yield (%)	M <sub>n</sub> <sup>c</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>
1	MoCl <sub>5</sub> / <i>n</i> -Bu <sub>4</sub> Sn (1:2)	toluene	30	24	1.0	0	-	-
2	WCl <sub>6</sub> /Ph <sub>4</sub> Sn (1:2)	toluene	30	24	1.0	0	-	-
3	WCl <sub>6</sub> /Ph <sub>4</sub> Sn (1:2)	dioxane	60	24	1.0	0	-	-
4	[(nbd)RhCl] <sub>2</sub> /Et <sub>3</sub> N (1:10)	THF	30	1	1.2	64	20,000	1.83
5	(nbd)Rh <sup>+</sup> ( <i>η</i> -Ph-B <sup>-</sup> Ph <sub>3</sub> )	THF	30	1	0.5	42	20,000	2.70
6	(nbd)Rh <sup>+</sup> ( <i>η</i> -Ph-B <sup>-</sup> Ph <sub>3</sub> )	THF	30	1	1.2	60	28,000	2.07
7	(nbd)Rh <sup>+</sup> ( <i>η</i> -Ph-B <sup>-</sup> Ph <sub>3</sub> )	THF	30	1	2.0	77	17,000	2.92
8	(nbd)Rh <sup>+</sup> ( <i>η</i> -Ph-B <sup>-</sup> Ph <sub>3</sub> )	THF	0	1	2.0	50	40,000	2.20
9	(nbd)Rh <sup>+</sup> ( <i>η</i> -Ph-B <sup>-</sup> Ph <sub>3</sub> )	THF	80	1	2.0	68	9,100	2.36
10	(nbd)Rh <sup>+</sup> ( <i>η</i> -Ph-B <sup>-</sup> Ph <sub>3</sub> )	THF	30	1	3.0	72	4,900	4.70

<sup>a</sup> [M]<sub>0</sub>/[Cat] = 100. <sup>b</sup> Methanol-insoluble product. <sup>c</sup> Estimated by GPC (THF, polystyrene standards). <sup>d</sup> Determined by <sup>1</sup>H NMR

While the  $M_n$  of poly(**2**) and poly(**3**) were no more than 5,100 and 5,000, respectively, poly(**4**) had a higher molecular weight ( $M_n = 26,000$ ). Although monomer **5** was completely soluble in THF, the resulting yellow polymer precipitated out during polymerization in THF; the polymer was insoluble in any organic solvents.

Table 2. Solvent effects on the polymerizations of **1** by  $(\text{nbD})\text{Rh}^+(\eta^6\text{-Ph-BPh}_3)^{\text{a}}$

Run	Solvent	Polymer <sup>b</sup>			
		Yield (%)	$M_n^c$	$M_w/M_n^c$	Cis <sup>d</sup> (%)
1	THF	77	17,000	2.92	75
2	toluene	71	10,000	3.70	32
3	CH <sub>2</sub> Cl <sub>2</sub>	46	9,500	6.49	55
4	CHCl <sub>3</sub>	51	10,000	3.78	50
5	anisole	89	10,000	11.0	45
6	dioxane	83	6,500	12.4	- <sup>e</sup>
7	DMSO	91	21,000	5.43	46
8	DMF	79	23,000	8.23	58
9	CH <sub>3</sub> CN	0	-	-	-

<sup>a</sup>Polymerized at 30 °C for 1 h.  $[\text{M}]_0 = 2.0 \text{ M}$ ,  $[\text{M}]_0/[\text{Rh}] = 100$ . <sup>b</sup>Methanol-insoluble product.

<sup>c</sup>Estimated by GPC (THF, polystyrene standards). <sup>d</sup>Determined by <sup>1</sup>H NMR. <sup>e</sup>Determination of the cis content was difficult for this sample because of the broad cis peak.

Table 3. Polymerization of **2–5** by  $(\text{nbD})\text{Rh}^+(\eta^6\text{-Ph-BPh}_3)^{\text{a}}$

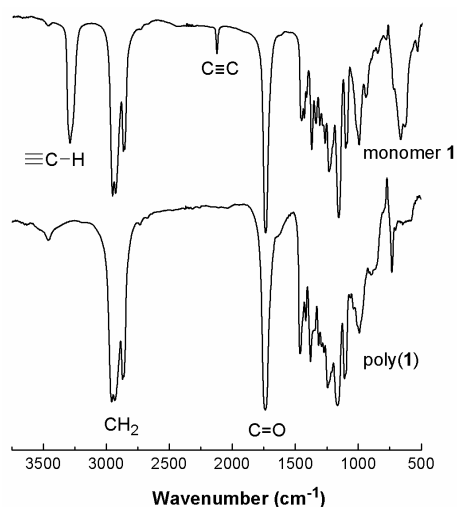
Monomer	Polymer <sup>b</sup>			
	Yield (%)	$M_n^c$	$M_w/M_n^c$	Cis <sup>d</sup> (%)
2	62	5,100 <sup>e</sup>	11.8 <sup>e</sup>	71
3	55	5,000	3.10	71
4	56	26,000	4.82	49
5	60	- <sup>g</sup>	- <sup>g</sup>	- <sup>g</sup>

<sup>a</sup>Polymerized in THF at 30 °C for 1 h,  $[\text{M}]_0 = 2.0 \text{ M}$ ,  $[\text{M}]_0/[\text{Rh}] = 100$ . <sup>b</sup>Methanol-insoluble product. <sup>c</sup>Estimated by GPC (THF, polystyrene standards). <sup>d</sup>Determined by <sup>1</sup>H NMR.

<sup>e</sup>Estimated by GPC (CHCl<sub>3</sub>, polystyrene standards). <sup>g</sup>Insoluble in common solvents.

### Polymer Structure

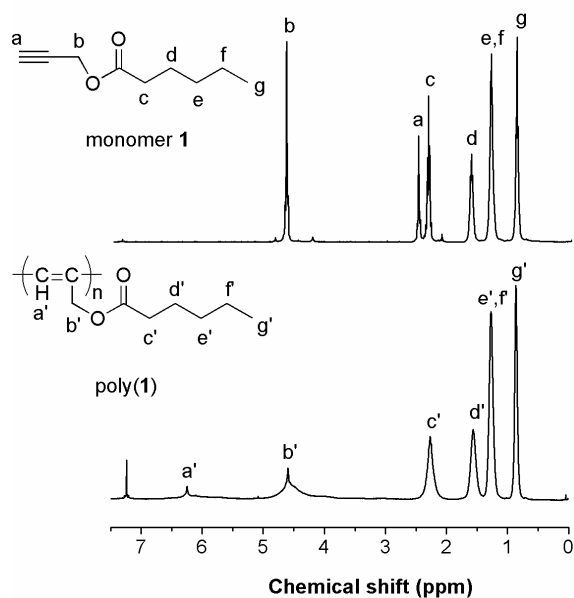
The structure of the polymers was elucidated by <sup>1</sup>H NMR and IR spectroscopies, and all the polymers gave satisfactory spectroscopic data corresponding to their expected molecular structures. IR spectra of monomer **1** and poly(**1**) are given as an example in Figure 1. Monomer **1** exhibits characteristic  $\equiv\text{C-H}$  and  $\text{C}\equiv\text{C}$  stretching vibrations at 3295 and 2129  $\text{cm}^{-1}$ , respectively, which completely disappear in the spectrum of



**Figure 1.** IR spectra of monomer **1** and poly(**1**) (KBr method; poly(**1**) sample from run 7, Table 1).

poly(**1**), indicating that the acetylene triple bond of **1** has been completely consumed by the polymerization reaction.

In the  $^1\text{H}$  NMR spectrum of poly(**1**), the peak due to acetylenic proton of **1** at 2.53 ppm completely disappeared and a new resonance peak assignable to the cis olefinic

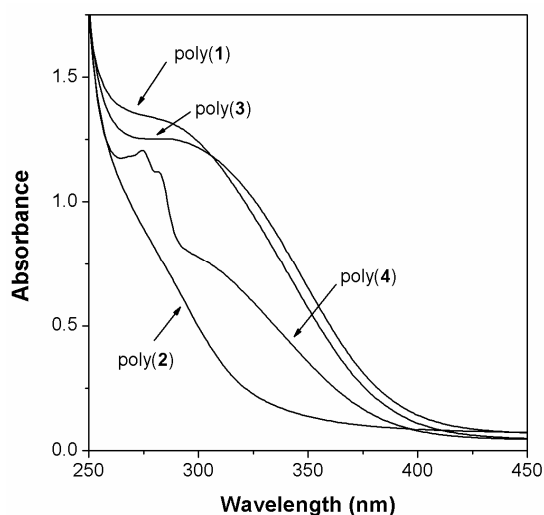


**Figure 2.**  $^1\text{H}$  NMR spectra of monomer **1** and poly(**1**) (measured in  $\text{CDCl}_3$ ; poly(**1**) sample from run 7, Table 1).

proton of polyene main chain appeared at 6.25 ppm, suggesting a cis-transoidal structure of the main chain [16]. The cis contents of poly(1)s in Tables 1 and 2 were estimated by the peak area ratio of olefinic protons of the main chain to methyl group in the pendant *n*-amyl group. It should be noted that the cis contents of poly(propargyl esters) in Tables 1–3 are lower than those (90–100%) of Rh-catalyzed substituted polyacetylene such as poly(phenylacetylene) [17] and poly(propargyl amides) [18], indicating that the present polymers have less stereoregularity of the polyacetylene backbone than other polymers. The signals characteristic of cis olefinic protons in the range of 6.26–6.44 ppm were also observed in the  $^1\text{H}$  NMR spectra of poly(2)–poly(4). By a method similar to that of poly(1), the cis contents of poly(2)–poly(4) were found to be in the range of 49–71% (Table 3). It has been reported that the peaks of cis protons in the  $^1\text{H}$  NMR spectrum of poly(*N*-propargylalkylamides) are very broad due to the limited main chain mobility [9]. On the contrary, the  $^1\text{H}$  NMR spectra of the present poly(propargyl esters) usually showed sharp signals of the cis protons, indicating that their main chain is enough flexible like those of poly(propionic esters) [19].

#### Polymer Properties

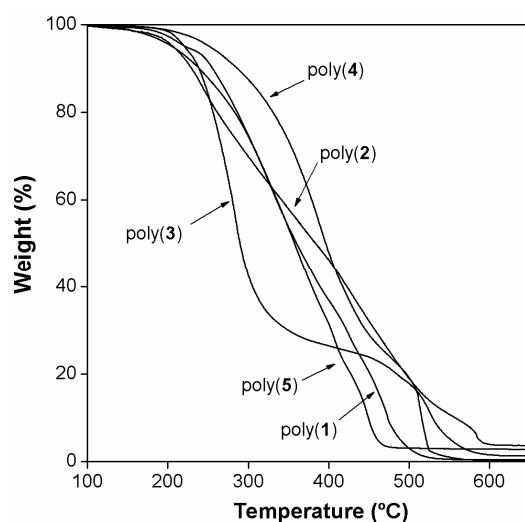
Poly(1) was viscous yellow oil owing to the presence of the long alkyl group (*n*-amyl) along the polymer main chain. Poly(2)–poly(5) were yellow solids. Figure 3 depicts the UV-vis spectra of poly(1)–poly(4). All the polymers exhibit absorptions in the range from 300 nm to 425 nm at longer wavelength region than their corresponding monomers. These absorptions are attributed to the conjugation of the main chain. The absorption of poly(2) is obviously located at shorter wavelengths than those of the other polymers, suggesting that the former has a shorter conjugation length than those of the latter. In the case of poly(4), the absorption peak at 256 nm in the ultraviolet region is associated with the pendant phenyl group.



**Figure 3.** UV-vis spectra of poly(1)–poly(4) in  $\text{CHCl}_3$  (concentration: 0.075 mg/mL; poly (1) from run 7, Table 1).



Poly(1), poly(3) and poly(4) were completely soluble in common organic solvents such as toluene, THF and  $\text{CHCl}_3$ . Poly(2) was soluble in toluene and  $\text{CHCl}_3$  but was insoluble in THF. Poly(5) was insoluble in common organic solvents, presumably owing to the bulky triphenylmethyl pendant group. The thermal stability of poly(1)–poly(5) was evaluated by the thermogravimetric analysis (TGA) (Figure 4). All the polymers started to lose weight from 150 to 200 °C. The temperatures for 5% weight loss in poly(4) and poly(5) were higher than those of poly(1)–poly(3), which shows that aromatic substituents impart thermal stability to the polymers. The temperature for 5% weight loss in poly(4) is around 250 °C, which is slightly higher than that of poly(phenylacetylene) (225 °C) [20].



**Figure 4.** TGA curves of poly(1)–poly(5) (measured in air; heating rate: 10 °C/min; poly (1) from run 7, Table 1).

## Conclusions

Polymerization of propargyl esters (1–5) in the presence of Rh catalysts afforded the corresponding polymers, poly(1)–poly(5), with  $M_n = 4,900$ –40,000. Poly(1), poly(3) and poly(4) were readily soluble in common organic solvents such as toluene, THF and  $\text{CHCl}_3$ , and poly(2) showed similar solubility property but was insoluble in THF. The  $^1\text{H}$  NMR spectra of the formed polymers exhibited signals in the range of 6.25–6.44 ppm assignable to the cis olefinic proton of polyacetylene main chain, indicating the cis-transoidal main-chain structure. The UV-vis spectra of poly(1)–poly(4) displayed absorptions in the region of 300–425 nm, which are attributed to the conjugation of the main chain.

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