

Polymerization of Substituted Acetylenes by the Grubbs–Hoveyda Ru Carbene Complex

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ABSTRACT: Polymerization of various mono- and disubstituted acetylenes was investigated by using Grubbs–Hoveyda catalyst (**1**). Hexyl propiolate (**2**) and 1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene (**3**) polymerized in moderate yields. Bulk polymerization of **2** at $[M]_0/[Ru] = 100$ and 80 °C for 24 h afforded poly(**2**) having $M_n = 25,500$ and $M_w/M_n = 2.63$. This polymer possessed relatively high *cis* content (75%) according to NMR. Monomer **3** polymerized in bulk to yield poly(**3**) with $M_n = 60,700$, $M_w/M_n = 2.22$ under conditions of 80 °C, 24 h, $[M]_0/[Ru] = 25$. The Ru-based poly(**3**) displayed a narrower conjugation than those obtained with other catalysts. The ¹³C NMR spectra of this polymer in solid and solution states showed quite different signal patterns from those with conventional catalysts, suggesting a different geometric structure of main chain. [DOI 10.1295/polymj.37.608]

KEY WORDS Substituted Polyacetylene / Ru Carbene Complex /

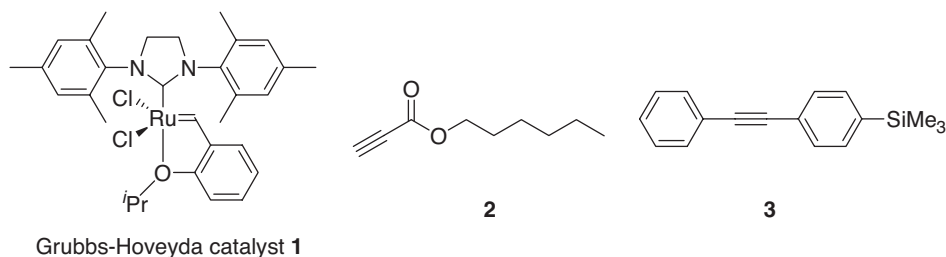
Substituted polyacetylenes have been gathering much attention due to their potential applications to material-separation membranes, and optoelectronic and related fields.¹ These polymers have been obtained by polymerization of corresponding acetylenic monomers in the presence of transition metal catalysts. Catalysts including group 5 and 6 transition metal and Rh have traditionally been employed to induce their polymerization. Among them, halides of early transition metals such as TaCl₅, NbCl₅, MoCl₅, and WCl₆ in conjunction with organometallic cocatalysts polymerize various mono- and disubstituted acetylenes to give high molecular weight polymers in good yield. Some well-defined Ta, Mo, and W carbenes, so-called Schrock carbenes, induce living polymerization of substituted acetylenes.^{2–5} This implies that the group 5 and 6 transition metal-catalyzed polymerization proceeds by the metathesis mechanism. One of the drawbacks of the early transition metal is that they are readily deactivated by polar groups in the monomer and polymerization solvents because of their high oxophilicity.

Another type of catalysts frequently used for the polymerization of substituted acetylenes are rhodium (Rh) catalysts. Rh catalysts can polymerize only monosubstituted acetylenes such as phenylacetylene and its ring-substituted derivatives,^{6–11} *N*-propargylamides,^{12–17} and propiolic esters.^{19–23} The Rh-catalyzed polymerization proceeds by the insertion mechanism, and features excellent tolerance to polar sub-

situents in the monomer^{24,25} and protic solvents.²⁶ The Rh-based polymers generally possess high *cis* stereoregularity, which is indispensable for the formation of helical structures of poly(*N*-propargylamide)s.^{12–17}

A huge number of studies on the synthesis and catalysis of ruthenium (Ru) carbene complexes have been reported in these several years. Ru carbene complexes represented by Grubbs' first- and second-generation catalysts exhibit high activity in olefin metathesis reactions such as ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM), cross metathesis (CM).²⁷ Compared to early transition metal-based metathesis catalysts, Ru carbene complexes display tolerance against protic functional groups in these metathesis reactions as well as considerable stability to oxygen and moisture. It should also be noted that many Ru complexes have well-defined carbene structures, which enables to directly generate carbene-type active species without adding cocatalysts. The Grubbs' second-generation complex reportedly reacts with diphenylacetylene stoichiometrically to afford η^3 -vinylcarbene complex, which is regarded as an intermediate of the polymerization of acetylenes.²⁸ Ru-catalyzed polymerizations of acetylene²⁹ and diyne compounds^{30,31} have recently been reported. Though an Ru carbene complex bearing 3-bromopyridine polymerizes not only acetylene but also its several derivatives, the substituted polyacetylenes formed have not been mentioned in detail.²⁹ Buchmeiser and coworkers developed living

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Chart 1.

polymerization systems by using diethyl dipropargylmalonate as monomer and mainly Ru carbenes containing trifluoroacetate ligands as catalysts.^{30,31} These facts prompted us to examine the polymerization of various mono- and disubstituted acetylenes by an active Ru carbene catalyst.

This paper reports on the polymerization of the substituted acetylenes using the Grubbs–Hoveyda Ru carbene (**1**)^{32–34} which is one of the most active Ru catalysts in metathesis reactions (Chart 1). Hexyl propiolate (**2**), 1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene (**3**), phenylacetylene, 1-octyne, etc. were used as monomers. Among these monomers, **2** and **3** afforded polymers in moderate yields in bulk polymerization. The geometric structure and properties of poly(**2**) and poly(**3**) were elucidated by NMR and other analytical methods.

EXPERIMENTAL

General

The molecular weights of polymers were estimated by gel permeation chromatography (THF as eluent, Showa Denko Shodex KF-805L×3, polystyrene calibration). IR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer. ¹H (400 MHz) and ¹³C NMR (100 MHz) spectra were measured in CDCl₃ solution on a JEOL EX-400 spectrometer. Chemical shifts (δ) for ¹H and ¹³C are referenced to internal solvent resonances and shown relative to tetramethylsilane. Thermogravimetric analyses (TGA) were conducted in air with a Perkin-Elmer TGA7 thermal analyzer. Ultraviolet–visible (UV–vis) and emission spectra were measured on Jasco V-550 and FP-750 spectrophotometers, respectively. 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 250 and 230 °C, respectively) using cyclododecane as an internal standard.

Solid-State ¹³C NMR Measurements (CP/MAS and CP+DDPh)

The ¹³C NMR spectra were recorded on a Bruker

Avance DSX300 NMR (75.6 MHz) spectrometer at room temperature. A conventional 4 mm wide-bore CP/MAS probehead was used; the contact time was 2 ms and the $\pi/2$ pulse width was 3.2 μ s for ¹H. The ¹³C chemical shifts were calibrated by using adamantane ($\delta = 29.5$ ppm) as an external standard relative to tetramethylsilane ($\delta = 0$ ppm).

Materials

Grubbs–Hoveyda catalyst **1** was offered by Materia (USA). TaCl₅ (Strem Chemicals), WCl₆ (Aldrich), MoCl₅ (Aldrich), MoOCl₄ (Aldrich), and WOCl₄ (Aldrich) as main catalyst components and Ph₄Sn (Wako Pure Chemical) as a cocatalyst were used without further purification. *n*-Bu₄Sn (Wako Pure Chemical) as a cocatalyst, and 1-octyne (TCI) and phenylacetylene (Aldrich) as monomers were purified by distillation. Monomers **2**,²¹ **3**,³⁵ *N*-propargylhexanamide,¹⁸ and [(*nbd*)RhCl]₂³⁶ were prepared according to the literature methods. Toluene, THF, 1,2-dichloroethane, and acetonitrile as solvents for polymerization were purified by distillation, and DMSO and ethyl acetate were used as received (Wako Pure Chemical).

Bulk Polymerization

Polymerizations were performed in a Schlenk tube equipped with a three-way stopcock under argon. Unless otherwise specified, the reactions were carried out for 24 h. The following procedure is exemplary: Monomer **2a** (0.15 g, 1.0 mmol) was added to a Schlenk tube that had been charged with catalyst **1** (6.3 mg, 10 μ mol) beforehand. Polymerization was carried out at 80 °C for 24 h. The formed polymer was dissolved in toluene (2.0 mL) and isolated by precipitation into a large excess of methanol, filtered, and dried under vacuum to constant weight. Its yield was determined by gravimetry.

Solution Polymerization

Unless otherwise specified, polymerizations were carried out in an argon atmosphere for 24 h under the following conditions: [M]₀ = 0.50 M, [Ru] = 10 mM. A detailed procedure of polymerization is as follows: A monomer solution was prepared in a Schlenk

Table I. Bulk polymerization of **2** by catalyst **1**

Run	Temperature (°C)	[M] ₀ /[Ru]	Time (h)	Polymer ^a		
				Yield (%)	<i>M</i> _n ^b	<i>M</i> _w / <i>M</i> _n ^b
1	60	100	24	12	43,400	2.48
2	80	100	24	24	25,500	2.63
3	120	100	24	0	(1900) ^c	(1.11) ^c
4	80	25	24	0	(1500) ^c	(1.05) ^c
5	80	50	24	5	20,900	1.86
6	80	200	24	23	21,500	2.65
7	80	200	168	28	23,800	2.35

^aMethanol-insoluble part. ^bMeasured by GPC. ^cMethanol-soluble part.

tube with a three-way stopcock by mixing monomer **2a** (0.15 g, 1.0 mmol) and toluene (1.0 mL), and another Schlenk tube was charged with catalyst **1** (13 mg, 20 μmol) and toluene (1.0 mL). Polymerization was initiated by adding the monomer solution to the catalyst solution, and continued at 60 °C for 24 h. Then the reaction was quenched by adding a small amount of methanol. The formed polymer was isolated by precipitation into a large excess of methanol, filtered, and dried under vacuum to constant weight, whose yield was determined by gravimetry.

RESULTS AND DISCUSSION

Polymerization of Monomer **2**

Bulk polymerization of monomer **2** was at first studied in detail (Table I). The effect of polymerization temperature was examined keeping at [M]₀/[cat] = 100 and time = 24 h. At 60 °C, polymer was obtained in 12% yield, whose *M*_n was 43,400 (run 1). With increasing temperature, the polymer yield tended to increase, while the *M*_n of polymer decreased. Thus, the polymer yield increased to 24% at 80 °C, while only methanol-soluble oligomers formed at 120 °C (runs 2, 3). Next, the [M]₀/[cat] ratio was varied while keeping the polymerization temperature at 80 °C. Even though [M]₀/[cat] ratio was increased to 200, no significant difference was observed in polymer yield and molecular weight (run 6). On the other hand, decreases in the [M]₀/[cat] ratio resulted in lower yields and *M*_n's (runs 4, 5). This suggests that methanol-soluble oligomers are mainly formed at high catalyst concentrations. The polymerization seems to level off after a certain period of time, because the polymer yield did not obviously increase even after 7 d (run 7).

Solution polymerization catalyzed by **1** proceeded with monomer **2**. Among toluene, THF, 1,2-dichloroethane, acetonitrile, ethyl acetate, and DMSO as polymerization solvents, toluene usually achieved the

Table II. Solution polymerization of **2** by catalyst **1**^a

Run	Temperature (°C)	Polymer ^b		
		Yield (%)	<i>M</i> _n ^c	<i>M</i> _w / <i>M</i> _n ^c
1	50	0	—	—
2	55	Trace	—	—
3	60	6	1,400,000 (14%) ^d	1.15
			32,900 (86%) ^d	1.87
4	65	4	41,000	3.47
5	70	13	37,500	2.61
6	80	18	19,900	2.60
7	90	0	—	—

^aPolymerized in toluene for 24 h; [Ru] = 10 mM, [M]₀ = 0.50 M. ^bMethanol-insoluble part. ^cMeasured by GPC. ^dPeak area ratio in GPC.

highest polymer yields. Detailed results using toluene as solvents are shown in Table II. Whereas only trace or no polymer was obtained at 55 °C and below in toluene (runs 1, 2), polymerization proceeded at 60 °C to give in 6% yield a polymer having bimodal MWD (*M*_n = 1,400,000 and 32,900, run 3). The polymer yield was improved by raising the polymerization temperature, while an adverse effect was observed for molecular weight. With increasing temperature, the bimodal peak in GPC chart changed into a single peak bearing a shoulder with wide polydispersity at 65 °C and a unimodal peak at 70 °C (runs 4, 5). The polymer yield increased to 18% at 80 °C (run 6) as in bulk polymerization, while no methanol-insoluble polymer was obtained at 90 °C (run 7).

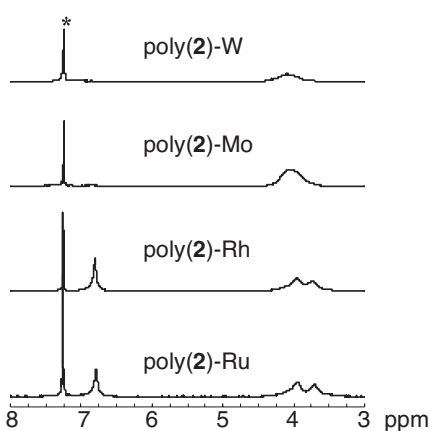
Structure and Properties of Poly(**2**)

It has been reported that monomer **2** can be polymerized by Rh, Mo, W catalyst systems and that the formed polymers possess different geometric structures depending on the catalysts used.²³ More specifically, the poly(propionic ester)s obtained with Rh catalysts have high *cis* contents, while *trans*-rich polymers are obtained with Mo and W catalysts. Actually poly(**2**) samples were prepared in this study by using [(nbd)RhCl]₂, MoOCl₄/*n*-Bu₄Sn, and WOCl₄/*n*-Bu₄Sn to compare the geometric structure with that obtained with Ru catalyst **1** (Table III), and the ¹H NMR spectra of the poly(**2**)s were depicted in Figure 1. In general, it is known that the polymerization of monosubstituted acetylenes using Rh catalysts provide the *cis*-transoidal polyacetylenes.³⁷ The poly(**2**) formed with catalyst **1** had relatively high *cis* content comparable to the Rh-based polymer (runs 1, 4), while those with Mo and W catalysts had much lower *cis* contents (runs 2, 3). It is noteworthy that, although the polymerizations with Ru, W, and Mo catalysts should all proceed *via* the metathesis mechanism, the *cis* content of the Ru-based polymer

Table III. Polymerization of **2** by various catalysts

Run	Catalyst	Polymer ^d			
		Yield (%)	M_n^e	M_w/M_n^e	<i>cis</i> content (%) ^f
1 ^a	[(nbd)RhCl] ₂	36	237,000 (88%) ^g	2.34	83
			8800 (12%) ^g	1.20	
2 ^b	MoOCl ₄ / <i>n</i> -Bu ₄ Sn	45	9900	1.53	— ^h
3 ^b	WOCl ₄ / <i>n</i> -Bu ₄ Sn	35	4500	1.30	— ^h
4 ^c	1	24	25,500	2.63	75

^aIn CH₃CN at 30 °C for 24 h; [Rh] = 10 mM, [M]₀ = 1.0 M. ^bIn toluene at 60 °C for 24 h; [Cat] = 20 mM, [*n*-Bu₄Sn] = 20 mM, [M]₀ = 0.50 M. ^cAt 80 °C for 24 h; neat, [M]₀/[Ru] = 100. ^dMethanol-insoluble part. ^eMeasured by GPC. ^fDetermined by ¹H NMR (in CHCl₃, at 50 °C). ^gPeak area ratio in GPC measurement. ^hThe signals of the main-chain olefinic proton were too broad and small; the *cis* contents are assumed to be lower than 60%.


Figure 1. ¹H NMR spectra of poly(**2**)s obtained with various catalysts (samples from Table III; measured in CDCl₃ at 50 °C).

was significantly higher than those of W- and Mo-based counterparts. This difference may be accounted for by the presence of bulky ligands in Ru catalyst **1**, which should control the geometric structure more strongly.

Polymerization of Monomer **3**

Although the polymerization of monomer **3** did not proceed in any of toluene, THF, 1,2-dichloroethene, acetonitrile, ethyl acetate, and DMSO as solvents, its bulk polymerization took place, and so it was examined under various conditions (Table IV). When [M]₀/[Ru] = 100, polymer was hardly obtained at 60 °C, while polymer with $M_n = 96,900$ was formed in 16% yield at 80 °C (run 2). With increasing temperature to 120 °C, the polymer yield did not change, but the molecular weight decreased to 12,300 (run 3). This is a similar tendency to the case of monomer **2**, and the optimal polymerization temperature is concluded to be 80 °C. When the [M]₀/[Ru] ratio was varied with keeping the polymerization temperature at 80 °C, the polymer yield improved to 42% at [M]₀/[Ru] = 25 (run 5). When the polymerization

Table IV. Bulk polymerization of **3** by catalyst **1**^a

Run	Temperature (°C)	[M] ₀ /[Ru]	Polymer ^a			
			Time (d)	Yield (%)	M_n^b	M_w/M_n^b
1	60	100	1	Trace	—	—
2	80	100	1	16	96,900	2.56
3	120	100	1	16	12,300	2.15
4	80	10	1	25	26,100	2.05
5	80	25	1	42	60,700	2.22
6	80	50	1	35	95,500	1.91
7	80	200	1	10	107,400	2.39
8	80	100	7	48	83,300	1.98
9	80	200	7	39	92,400	2.01

^aFor 24 h. ^bMethanol-insoluble part. ^cMeasured by GPC.

time was extended to 7 d at [M]₀/[Ru] = 100 and 200, the polymer yield increased up to 48 and 39%, respectively (runs 8, 9).

The time course of the polymerization of monomer **3** by **1** is shown in Figure 2. Both monomer conversion and polymer yield leveled off after 24 h. The M_n reached 99,000 in 1 h and then somewhat decreased, while the polydispersity slightly increased.

Structure and Properties of Poly(**3**)

Poly(**3**) samples were synthesized by using various catalysts to study the polymer structure; the results of the polymerizations are shown in Table V.^{35,38} Whereas the Ta-, Mo-, and W-based polymers had colors of yellow to orange-yellow, only the Ru-based samples were virtually white in the powdery state. For the sake of comparison, poly(DPA) (DPA: diphenylacetylene) samples were also prepared, as is listed in Table V.

Figure 3 shows the IR spectra of monomer **3** and the four poly(**3**) samples. A peak at 1530 cm⁻¹ which is absent in the spectrum of monomer **3** appears in those of poly(**3**)s. This peak is assignable to the stretching vibration of alternating C=C bonds in the

Table V. Polymerization of **3** and DPA by various catalysts

Run	Monomer	Catalyst	Polymer ^d			
			Yield (%)	M_n^e	M_w/M_n^e	Color
1 ^a	3	TaCl ₅ / <i>n</i> -Bu ₄ Sn	80	70,200	3.14	Orange-yellow
2 ^a	3	MoCl ₅ /Ph ₄ Sn	21	48,900	10.5	Dark yellow
3 ^a	3	WCl ₆ /Ph ₄ Sn	29	11,200	2.31	Bright yellow
4 ^b	3	1	42	60,700	2.22	White
5 ^a	DPA	TaCl ₅ / <i>n</i> -Bu ₄ Sn	47	insoluble ^f	—	Yellow
6 ^c	DPA	1	22	insoluble ^f	—	White

^aIn toluene at 80 °C for 24 h; [Cat] = 20 mM, [Sn] = 40 mM, [M]₀ = 0.20 M. ^bAt 80 °C for 24 h; neat, [M]₀/[Ru] = 25. ^cAt 80 °C for 24 h; neat, [M]₀/[Ru] = 100. ^dMethanol-insoluble part. ^eMeasured by GPC. ^fInsoluble in any organic solvents including CHCl₃, toluene, and THF.

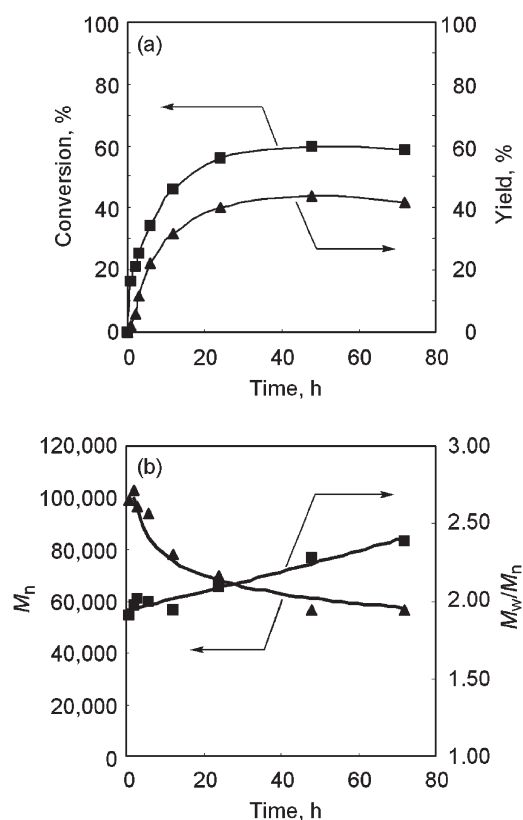


Figure 2. Time profile of the bulk polymerization of monomer **3** by **1**. (polymerized in toluene at 80 °C; [M]₀/[Ru] = 25; the polymer yield denotes the yield of methanol-insoluble part.)

main-chain which are generated by polymerization of the acetylene moiety. Slight differences are seen in the ranges of 500–700, 900–1100 and 1300–1750 cm⁻¹ in the four spectra of poly(**3**)s, which appears to reflect differences in the structure of the polymers.

As seen in Figure 4, the ¹³C NMR spectra of Ta-, W-, and Mo-based poly(**3**)s in CDCl₃ solution display seven peaks in the C_{sp²} region; *i.e.* sharp peaks at 126, 127 and 128 ppm, a large peak with a shoulder at 131 ppm, a small peak at 136 ppm and two sharp peaks at 144 and 146 ppm. These spectra are very similar to one another. On the other hand, the spec-

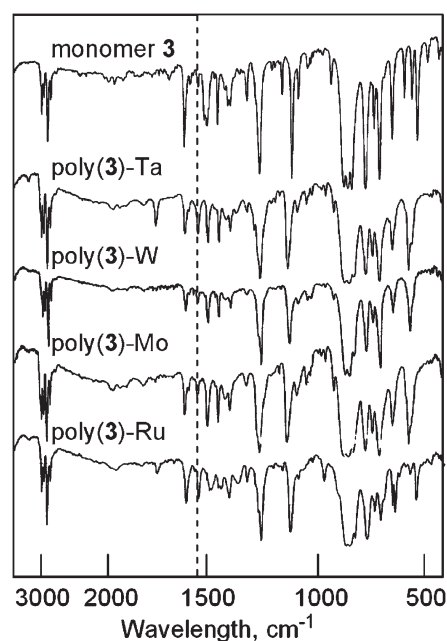


Figure 3. IR spectra (KBr pellet) of poly(**3**)s obtained with various catalysts (samples from Table V). Dot line is 1530 cm⁻¹.

trum of the Ru-based poly(**3**) is quite different from those of the other three polymers. This indicates that the Ru-based polymer has a different structure from those of the other polymers, but the detailed difference is not clear from these spectra.

Whereas the UV/vis spectra of poly(**3**)s obtained with the conventional catalysts display two peaks around 375 and 435 nm, that of the polymer with catalyst **1** possessed only one peak at 290 nm (Figure 5a). This indicates that the conjugation length of the latter polymer is much shorter than those of the former polymers. The fluorescence spectra of poly(**3**)s excited at their absorption maxima were shown in Figure 5b. The fluorescence spectra of the former three polymers are similar to one another, while that with catalyst **1** is quite different.

The TGA curves of these poly(**3**)s measured in air are more or less different from one another. According

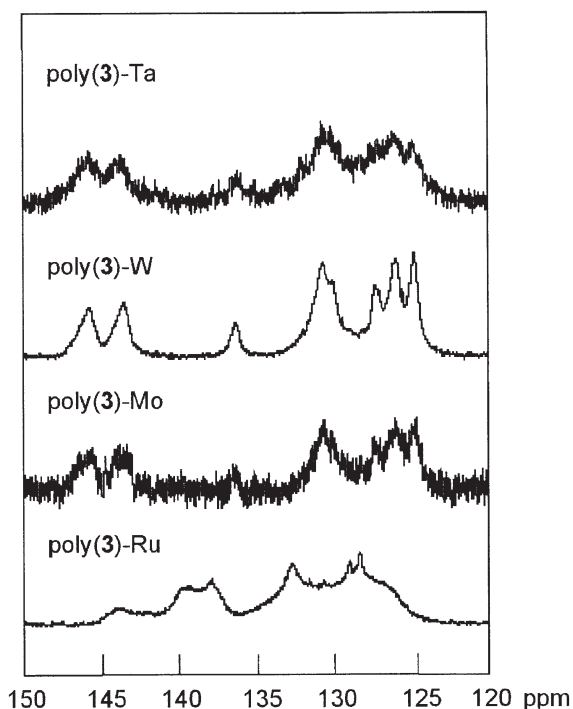


Figure 4. ^{13}C NMR spectra of poly(3)s obtained with various catalysts (samples from Table V; measured in CDCl_3 at room temperature).

the onset temperature (T_0) of weight loss, the polymers with Ta and Mo ($\sim 450^\circ\text{C}$) are more stable than those with Ru and W ($\sim 350^\circ\text{C}$) (Figure 6). Furthermore, the Ru-based polymer loses weight steeply with increasing temperature. While the rather low T_0 of the Ru-based polymer should be due to the difference in polymer structure from other polymers, that of the W-based polymer may stem from its low molecular weight. The residue at around 700°C is attributed to SiO_2 whose weight is theoretically 24% of the polymer.

All of the poly(3) samples were totally soluble in toluene, THF, and chloroform (Table VI). Among these samples, some differences were observed; the Ta-based polymer was insoluble in hexane, the Mo-based one was partly soluble, and the W- and Ru-based ones were completely soluble.

Solid-State ^{13}C NMR

The solid-state ^{13}C NMR spectra of a series of poly(3)s were measured in order to gain more detailed information about polymer structure. The spectra of poly(DPA)s synthesized with both $\text{TaCl}_5/n\text{-Bu}_4\text{Sn}$ and Ru catalyst **1** were also studied for comparison because poly(DPA) is not accompanied by the problem of head-to-tail and head-to-head. Figure 7 exhibits the 110–160 ppm region of the ^{13}C CP/MAS spectra of poly(3)s and poly(DPA)s. The spectra of poly(3) and poly(DPA) obtained with the Ta catalyst resemble each other. The same thing can be said with poly(3)

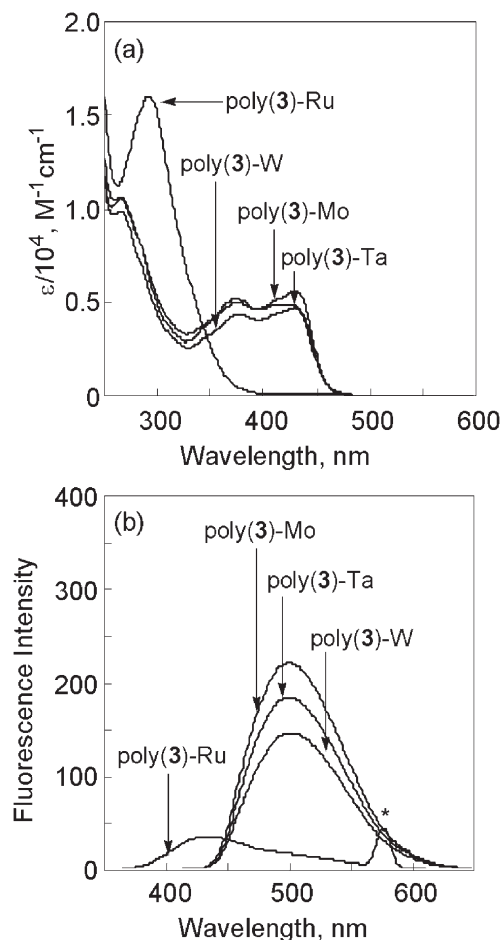


Figure 5. (a) Uv-vis spectra of poly(3)s obtained with various catalysts (samples from Table V; measured in CHCl_3 , $c = 1.0 \times 10^{-4}$ M). (b) Fluorescence spectra of poly(3)s obtained with various catalysts (samples from Table V; measured in CHCl_3 ; excited at 292 nm (Ru), 374.5 nm (Mo), or 376 nm (Ta, W); $c = 1.0 \times 10^{-5}$ M). Asterisked is an optical ghost peak.

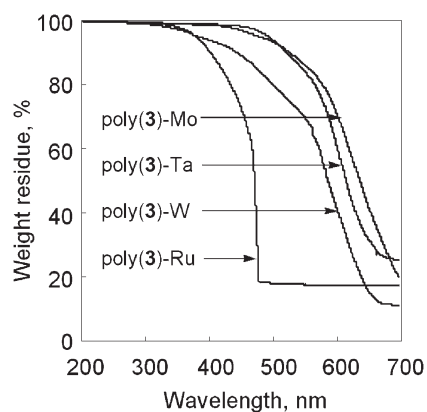


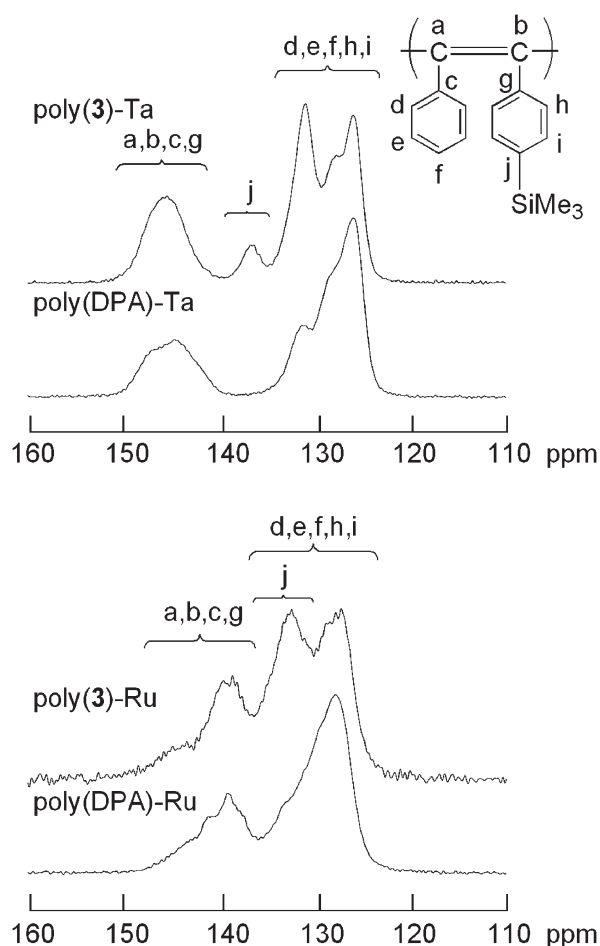
Figure 6. TGA curves of poly(3)s obtained with various catalysts (samples from Table V; measured in air; heating rate $10^\circ\text{C}/\text{min}$).

and poly(DPA) formed with Ru catalyst **1**. Since poly(DPA) does not involve the problem of regio-regularity, the difference in the spectra of the poly-

Table VI. Solubility of poly(**3**) obtained with various catalysts

Solvent	Poly(3)			
	TaCl ₅ / <i>n</i> -Bu ₄ Sn	MoCl ₅ /Ph ₄ Sn	WCl ₆ /Ph ₄ Sn	Ru cat. (1)
DMSO	—	—	—	—
DMF	—	±	±	±
Acetone	—	±	±	±
CH ₂ Cl ₂	+	+	+	+
THF	+	+	+	+
<i>o</i> -Dichlorobenzene	+	+	+	+
Chlorobenzene	+	+	+	+
CHCl ₃	+	+	+	+
Anisole	+	±	+	+
Et ₂ O	+	+	+	+
Benzene	+	+	+	+
Toluene	+	+	+	+
CCl ₄	+	+	+	+
Cyclohexane	+	+	+	+
Hexane	—	±	+	+

+: soluble; ±: partly soluble; —: insoluble.

**Figure 7.** ¹³C CP/MAS spectra of poly(**3**)s and poly(DPA)s.

mers with catalysts is attributable to the difference in the main-chain configuration.

The ¹³C CP+DDPh (dipolar dephasing)/MAS experiments were performed to assign each peak in

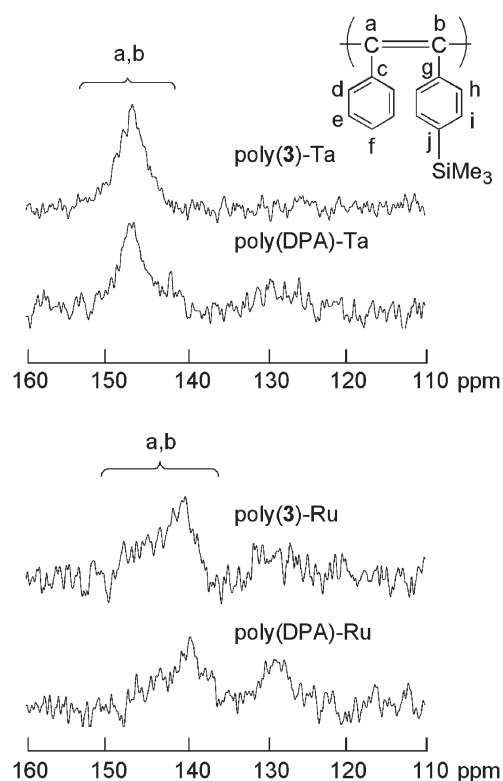
**Figure 8.** ¹³C CP+DDPh/MAS spectra of poly(**3**)s and poly(DPA)s (the dephasing time 100 μs).

Figure 7. Dipolar dephasing spectra were observed by inserting a dephasing period between the CP period and detection. When the dephasing time was 100 μs, the Ta-based poly(**3**) displayed relatively strong peaks around 146 ppm, while the Ru-based poly(**3**) displayed a relatively broad peak around 140 ppm with a shoulder positioning at 145 ppm (Figure 8). These peaks are generally assigned to the carbons that do

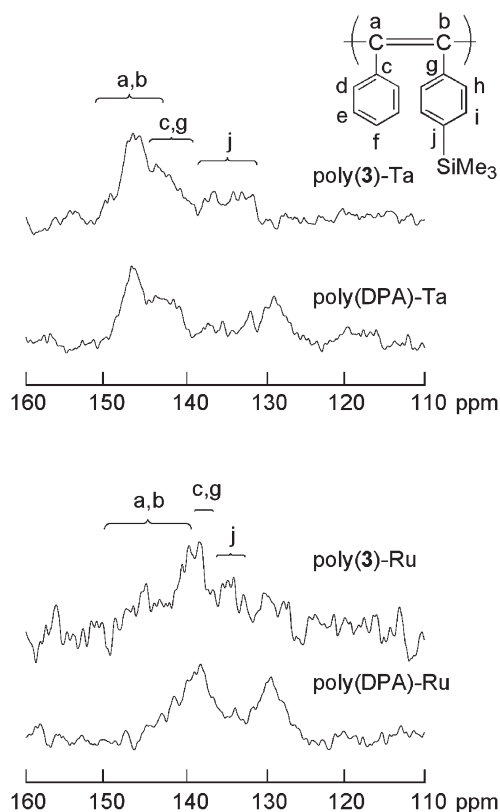


Figure 9. ^{13}C CP+DDPh/MAS spectra of poly(3)s and poly-(DPA)s (the dephasing time 60 μs).

not have strong interaction with hydrogen atoms, and thus should be derived from main-chain carbon atoms of each polymer. By adopting a dephasing time of 60 μs , new peaks appeared at a higher magnetic field (Figure 9). Namely, two peaks were newly observed at 142 ppm as a shoulder and at 136 ppm in Ta-based poly(3), and at 138 and 134 ppm in Ru-based poly(3). These peaks can be assigned to the substituted carbons of the phenyl rings. Further, when compared with the spectra of poly(DPA), the peaks at 142 and 136 ppm in the Ta-based poly(3) are assigned to the benzene carbons attached to the main chain and the silyl group, respectively; on the other hand, the peaks at 138 and 134 ppm in the Ru-based poly(3) are based on the benzene carbons attached to the main chain and the silyl group, respectively. From the above discussion, the signals of ^{13}C NMR spectra are assigned as shown in Figure 7. It is noteworthy that not only the main-chain carbons but also benzene carbons exhibit different chemical shifts depending on the kind of catalysts used. Further, it is noted that the Ru-based polymers have a broader distribution in the main-chain configuration according to the signals of the 146–140 ppm region. At this moment, we can say from the solid-state ^{13}C NMR spectra that the Ru- and Ta-based poly(3)s have clearly different geometric structures in the main chain to each other.

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