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Polymerization of *o*-diethynylbenzene and its derivatives controlled by transition metal catalyst systems

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Abstract

Polymerization of *o*-diethynylbenzene (**1**) by Rh and Ta catalysts resulted in the formation of structurally different polymers depending on the kind of catalyst. When a Rh catalyst was used, insoluble cross-linked poly(**1**) was formed, mainly consisting of alternating double bonds and the unreacted ethynyl group along with indene-type structure formed by intramolecular cyclization as a minor component. A Ta catalyst completely consumed both ethynyl groups in the polymerization of **1** to afford mainly highly cross-linked poly(**1**) containing trisubstituted benzene unit via intermolecular cyclization. 1-Ethynyl-2-phenylethynylbenzene (**2**) was polymerized by W and Mo catalysts to give soluble polymers with M_n of 6300–71,900 in good yields. Poly(**2**) obtained by Mo catalysts had alternating double bonds in the main chain and *o*-(phenylethynyl)phenyl group as side chains. Poly(**2**) formed by W catalysts predominantly contained a similar main-chain structure and also possessed the naphthalene-type cyclic unit formed by cyclization of the adjacent diethynyl groups as a minor part.

Keywords: *o*-Diethynylbenzene; Polymerization; Transition metal catalyst

1. Introduction

Enediynes are versatile building blocks in organic chemistry, which can be converted to various conjugated moieties in compounds such as 5- or 6-membered rings [1,2]. Enediynes react in the presence of transition metal catalysts to give a variety of conjugated structures, which complicates their polymerization behavior. Enediynes represented by *o*-diethynylbenzene (**1**) and its derivatives such as 1-ethynyl-2-phenylethynylbenzene (**2**) are known to polymerize via thermal intramolecular cyclization, the so-called Bergman cyclopolymerization [3–5]. The structure of the formed polymer mainly consists of 1,4-benzene or naphthalene moieties, which are formed through 1,4-diradical intermediate. However, the main-chain of the polymer always involves a significant amount of unidentified structural units. Recently, Matzger and coworkers revealed that the polymer obtained by Bergman cyclopolymerization (route a, Scheme 1) of *o*-diethynylbenzene contains not only 1,4-naphthalene blocks but also indenes as well as alternative double bonds similarly to poly(phenylacetylene) possessing intact *o*-ethynyl group [6]. On the other hand, there are only two reports dealing with the use of transition metal catalyst systems for the polymerization of **1**. Aso and coworkers found that Ziegler-type Ti/Al catalysts are effective for the polymerization of **1**, but the structure of the formed polymer was not clearly elucidated [7]. Kim et al. reported that, in the polymerization of **1** with $MoCl_5$-based catalysts, both ethynyl groups of **1** are completely consumed to form a polymer containing five-membered ring, namely, indenes, in the main chain (route b, Scheme 1) [8].

Because **1** has two neighboring ethynyl groups, it is interesting to study the polymerization of **1** by using various transition metal catalysts for the synthesis of substituted polyacetylenes, which may lead to polymers with different structures and properties [9]. Moreover, **1** is expected to undergo the Ta-catalyzed diyne polycyclotrimerization to give highly conjugated polymer [10]. Here, we present our findings concerning the polymerization of **1** and its derivatives, 2 and *o*-diphenylethynylbenzene (**3**) by Rh, Mo, W, and Ta catalysts, and elucidation of the structures of the polymers formed by these catalysts.

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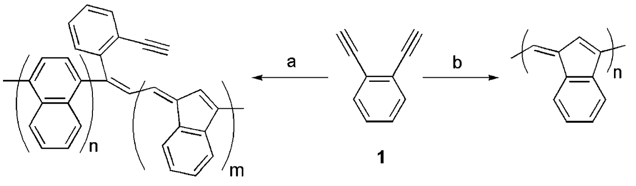


a) in toluene, 170 °C (Bergman cyclopolymerization) [6].
b) WCl_6- or $MoCl_5$-based catalyst, in toluene, 30 or 60 °C [8].

Scheme 1. Polymerization of *o*-diethynylbenzene (**1**).

2. Experimental section

2.1. Materials

$TaCl_5$, WCl_6, $MoCl_5$, Ph_4Sn, and triethylamine (Et_3N) were purchased and used without further purification. Toluene, tetrahydrofuran (THF), and *n*-Bu_4Sn were purified by distillation before use. Monomers **1** [3], **2** [3], **3** [3], and $[(nbd)RhCl]_2$ (nbd = 2,5-norbornadiene) [11] were prepared according to the methods described in the literature.

2.2. Instrumental measurements

^1H and ^{13}C NMR spectra were recorded in chloroform ($CDCl_3$) on a JEOL EX-400 spectrometer. IR spectra were measured using a Shimadzu FTIR-8100 spectrophotometer. The number- and weight-average molecular weights (M_n and M_w) 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 THF as an eluent at a flow rate of 1.0 mL/min, calibrated by polystyrene standards at 40 °C. Thermogravimetric analyses (TGA) were conducted on a Perkin–Elmer TGA thermal analyzer. UV–vis spectra were recorded on a Shimadzu UV-2200 spectrophotometer. Samples were pyrolyzed with a Japan Analytical Industry JHP-5 at 740 °C for 5 s, followed by separation with an J and W DB-5MS column (30 m × 0.25 mm × 0.25 μm) equipped in Shimadzu GC-17A with a temperature gradient (40 °C for 3 min, ramped at 10 °C per min to 320 °C, and held for 12 min) and analyzed by a Shimadzu QP-5000C mass spectrometer.

2.3. 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. This catalyst solution was aged at 60 °C (for Mo and W) or 80 °C (for Ta) for 10 min. In the case of Rh catalyst, the catalyst solution was prepared without the aging process. Then the monomer solution was added to the catalyst solution, and polymerizations were carried out for given times at given temperatures. Polymers were collected by precipitation in methanol and dried in vacuo overnight. The yields of the polymers were determined by gravimetry.

3. Results and discussion

3.1. Polymerization of *o*-diethynylbenzene (*1*)

The polymerization of **1** was examined by using Rh and Ta catalysts, whose results are summarized in Table 1. The binary $[(nbd)RhCl]_2/Et_3N$ catalyst, which is usually active for the polymerization of monosubstituted acetylenes, produced poly(**1**)s in 18 and 21% yield at 30 °C in THF and toluene, respectively, (runs 1 and 2). Both of the formed poly(**1**)s were yellowish brown and insoluble in common organic solvents such as THF, $CHCl_3$, and toluene. Since toluene gave the polymer in a relatively high yield, the following polymerizations were carried out in toluene as solvent. The polymer yield increased at 60 °C with increasing catalyst amount. When the mole ratio of $[(nbd)RhCl]_2$ to Et_3N was changed from 1:10 to 1:4, the polymer yield increased. When the polymerization was carried out at 80 °C at $[(nbd)RhCl]_2/Et_3N$ = 1:4, a higher yield up to 73% was achieved. A 1:2 mixture of $TaCl_5$ and Ph_4Sn, which is an effective binary catalyst for the polycyclotrimerization of diynes [10], was also employed in

Table 1
Polymerization of *o*-diethynylbenzene **1**

Run	Catalyst	$[M]_0/[Cat.]$	Solvent	Temp. (°C)	Yield (%)[a]	D_{3289}/D_{3040}[b]	Remaining $C\equiv C$ (%)[c]
1	$[(nbd)RhCl]_2/Et_3N$ (1:10)[d]	100	THF	30	18	1.40	64
2	$[(nbd)RhCl]_2/Et_3N$ (1:10)	100	Toluene	30	21	1.60	73
3	$[(nbd)RhCl]_2/Et_3N$ (1:10)	50	Toluene	60	40	1.30	60
4	$[(nbd)RhCl]_2/Et_3N$ (1:4)	50	Toluene	60	49	1.34	61
5	$[(nbd)RhCl]_2/Et_3N$ (1:4)	50	Toluene	80	73	1.12	50
6	$TaCl_5/Ph_4Sn$ (1:2)	50	Toluene	80	79	0	0
7	$TaCl_5/Ph_4Sn$ (1:2)	25	Toluene	80	91	0	0

Twenty-four hour, $[M]_0$ = 0.50 M.
[a] Methanol-insoluble part.
[b] Determined by IR spectra (KBr disc) according to the Ref. [7].
[c] Reaction time: 48 h.
[d] Mole ratio.

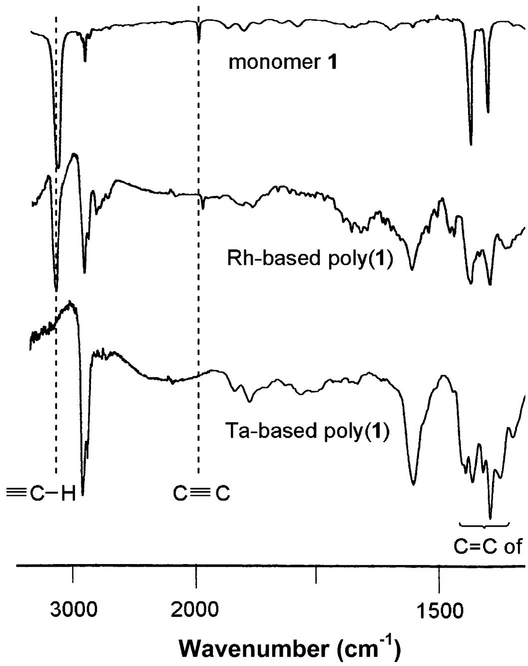


Fig. 1. IR spectra of monomer **1** and poly(**1**)s obtained with $[(nbd)RhCl]_2/Et_3N$ (sample from Table 1, run 4) and $TaCl_5/Ph_4Sn$ (Table 1, run 7), respectively.

the polymerization of **1** (runs 6 and 7). The reaction proceeded rapidly to form a dark brown precipitate. The precipitate was poured into methanol and an insoluble product was obtained in a high yield after subsequent drying to a constant weight.

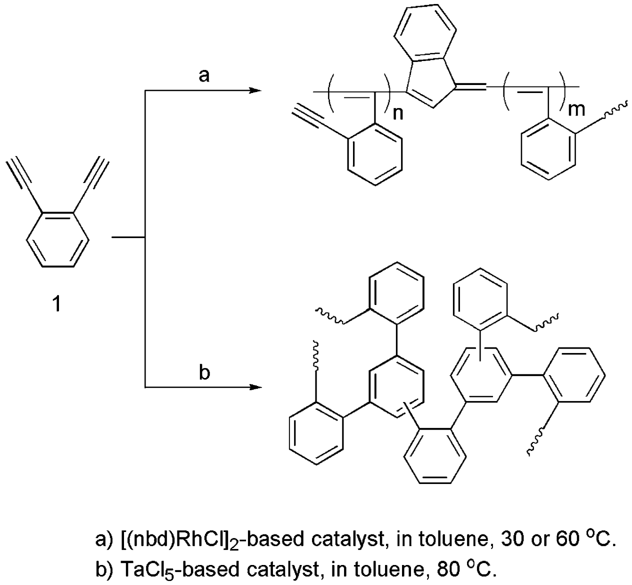
3.2. *Structure of poly(**1**)*

Like poly(**1**)s previously obtained by Bergman cyclization [6] and W- or Mo-catalysts [8], the present poly(**1**)s were insoluble in any organic solvents, suggesting that they were cross-linked. The structures of the formed polymers were analyzed by IR, pyrolysis GC-MS, and thermogravimetric analysis (TGA) measurements.

Fig. 1 shows the IR spectra of Rh- and Ta-based poly(**1**) (runs 3 and 7, respectively, in Table 1), as well as of monomer **1**. By comparison with the spectrum of the monomer, the absorption peaks of Rh-based poly(**1**) at 3289 and 2110 cm^{-1} can be ascribed to the C–H and C≡C stretchings, respectively, of the terminal acetylene. This means that the unreacted second ethynyl group of **1** is remaining in the polymer. Also et al. calculated the amount of remaining ethynyl group from the ratio of the peak intensities at 3289 cm^{-1} (terminal acetylene C–H) and 3063 cm^{-1} (aromatic C–H) [7]. The amounts of remaining ethynyl group in the present Rh-based poly(**1**) were estimated by applying the same method, which are presented in Table 1. In contrast, the IR spectra of the Ta-based poly(**1**)s displayed no peaks around 3290 and 2100 cm^{-1}, suggesting that ethynyl groups were completely consumed. The observed spectra also showed many peaks in the region 1600–1420 cm^{-1}, which are assigned to aromatic C–C bond stretchings.

IR analysis was useful for the detection of remaining ethynyl group in the polymers. Further, structural information were obtained by the pyrolysis GC-MS analysis [6,12]. Rh- and Ta-based poly(**1**)s underwent rapid pyrolysis, and subsequently the decomposition products were separated by chromatography and analyzed by mass spectrometry. Rh-based poly(**1**) (run 4, Table 1) pyrolyzed at 590 °C gave rise to three types of molecular species; i.e. (i) benzene (16.2%) and toluene (30.7%), (ii) indene derivatives such as indene (5.2%) and methyleneindene (4.9%), and (iii) polycyclic aromatic compounds such as benzo[a]anthracene, chrysene and their derivatives (43.1%). The presence of a small amount of five-membered rings (indene) in the polymer suggests that a portion of **1** was subjected to intramolecular cyclization, as in the cases of Bergman polymerization [6] and Mo/W-catalyzed polymerization of **1** [8]. When this poly(**1**) was pyrolyzed at 740 °C, the compounds obtained were the same but the proportion of the polycyclic aromatic compounds increased; i.e. benzene (9.2%) and toluene (13.9%), indene derivatives such as indene (3.2%) and methyleneindene (3.4%), and polycyclic aromatic compounds (70.3%). Thus, the compositions of decomposition products at 590 and 740 °C were different. This finding suggests that those polycyclic moieties might be formed by the decomposition of main- and side-chains of the polymer followed by the cyclization of the remaining conjugated moieties. It is noteworthy that naphthalene and its derivatives were not detected in Rh-based poly(**1**) at either temperature, which were observed in Bergman polymerization of **1** [6]. This observation excludes the possibility of head-to-head intramolecular cyclization. Based on these results, it is proposed that Rh-based poly(**1**) has a cross-linked structure with an unreacted ethynyl group partially appended to the polymer chain, as well as a minor amount of five-membered rings (route 1, Scheme 1).

Pyrolysis GC-MS analysis of Ta-based poly(**1**) (run 7, Table 1) displayed a relatively simple product distribution. In the pyrolysis at 740 °C, a large portion of the decomposition products was mononuclear aromatic compounds such as



a) $[(nbd)RhCl]_2$-based catalyst, in toluene, 30 or 60 °C.
b) $TaCl_5$-based catalyst, in toluene, 80 °C.

Scheme 2. Polymerization of *o*-diethynylbenzene (**1**).

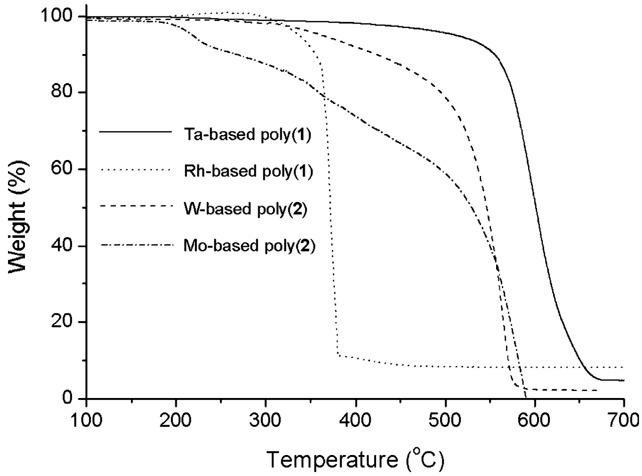


Fig. 2. TGA curves of Rh-based (sample from Table 1, run 4) and Ta-based poly(**1**) (Table 1, run 7); Mo-based (Table 2, run 3) and W-based poly(**2**) (Table 2, run 8) (measured in air; heating rate: 10 °C/min).

benzene (63.1%) and toluene (23.3%). Meanwhile, small amounts of biphenyl (8.9%) and terphenyls probably including 1,2,4- and 1,3,5-substituted isomers (4.7%) were also observed. Neither naphthalene nor indene was detected, which rules out the possibility of intramolecular cyclization of the monomer. As mentioned previously, $TaCl_5/Ph_4Sn$ is known as effective catalyst in the polycyclotrimerization of diynes, and hence the predominant amount of benzene rings and its derivatives in Ta-based poly(**1**) compared to Rh-based poly(**1**) possibly involves the benzene rings newly formed by Ta-catalyzed cyclotrimerization in addition to the benzene rings present in monomer **1** (route b, Scheme 2).

To further clarify their structural difference, the thermal stability of Rh- and Ta-based poly(**1**)s was examined by the thermogravimetric analyses (TGA) in air (Fig. 2). The onset temperature of Rh-based poly(**1**) was 300 °C and the temperature of 10% weight loss was around 350 °C. In contrast, Ta-based poly(**1**) exhibited outstanding thermal stability, losing only 5% weight at 550 °C in air, which is consistent with the hyperbranched polyphenylenes prepared by Ta-catalyzed polycyclotrimerization of diynes [10]. The high thermal stability is attributable to the highly cross-linked structure composed of benzene rings.

3.3. Polymerization of o-diethynylbenzene derivatives

As mentioned above, 1-ethynyl-2-phenylethynylbenzene (**2**), one of *o*-diethynylbenzene derivatives, is also known to undergo Bergman cyclopolymerization through intramolecular cyclization [3,4]. It was interesting for us to investigate the possibility of intramolecular cyclization of **2** induced by transition metal catalysts.

Table 2 summarizes the results of the polymerization of **2** with Rh, Ta, W and Mo catalysts in toluene at 30–80 °C for 24 h. Among Mo-catalyzed polymerizations, even $MoCl_5$ alone gave a polymer in a good yield (71%), although the molecular weight was relative low ($M_n=6600$). The addition of *n*-Bu_4Sn as co-catalyst slightly enhanced the catalytic activity, increasing both the yield (79%) and molecular weight ($M_n=30{,}000$) of poly(**2**). On the other hand, Ph_4Sn significantly increased M_n from 6600 to 71,900, although the polymer yield appreciably decreased (29%). In W-catalyzed polymerization, *n*-Bu_4Sn and Ph_4Sn were less effective as co-catalysts under the same conditions, giving polymers with low molecular weights. The increase in the polymerization temperature from 30 to 60 °C was effective to increase molecular weight. It is known that Rh catalysts are not very effective for the polymerization of sterically crowded *o*-substituted phenylacetylenes [9]. This explains why the use of $[(nbd)RhCl]_2/Et_3N$ as a catalyst resulted in a low-molecular-weight product ($M_n=1300$). A Ta-based catalyst, $TaCl_5$/*n*-Bu_4Sn, was also examined in the polymerization, but it was inactive to give a polymer with a high molecular weight ($M_n=1500$). This is probably due to the presence of two reactive triple bonds in **2**, which may give rise to bidentate coordination to make the catalytic species inactive for polymerization. The products obtained with W and Mo catalysts were yellowish brown in color and readily soluble in organic solvents such as THF, $CHCl_3$ and toluene. Further, the polymerization of monomer **3** by using W and Ta catalysts did not proceed at all.

Table 2
Polymerization of 1-ethynyl-2-phenylethynylbenzene **2**

Run	Catalyst	Temp. (°C)	Yield (%)[a]	M_n[b]	M_w/M_n[b]
1	$MoCl_5$	30	71	6600	2.25
2	$MoCl_5$/*n*-Bu_4Sn (1:2)	30	79	30,000	2.19
3	$MoCl_5/Ph_4Sn$ (1:2)	30	29	71,900	1.95
5	WCl_6	30	56	8000	1.71
6	WCl_6/Ph_4Sn (1:2)	30	66	6300	3.23
7	WCl_6/*n*-Bu_4Sn (1:2)	30	56	9900	1.80
8	WCl_6/Ph_4Sn (1:2)	60	80	24,300	1.81
9	WCl_6/*n*-Bu_4Sn (1:2)	60	80	23,800	1.95
10	$[(nbd)RhCl]_2/Et_3N$ (1:4)	60	33	1300	2.63
11	$TaCl_5$/*n*-Bu_4Sn (1:4)	80	57	1500	1.58

In toluene, 24 h, $[M]_0=0.50$ M, [cat.] = 20 mM.

[a] Methanol-insoluble part.

[b] Estimated by GPC (THF).

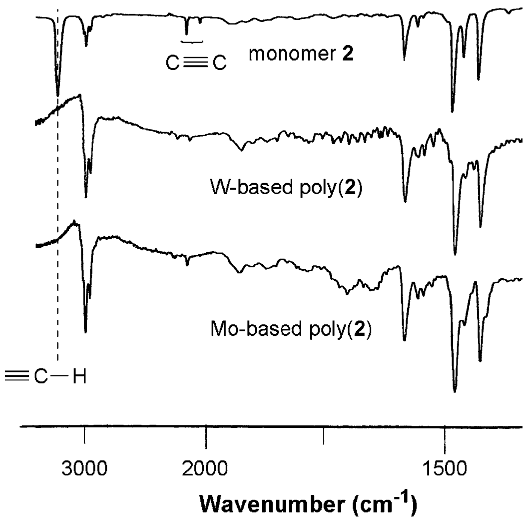


Fig. 3. IR spectra of monomer **2** and poly(**2**)s obtained with MoCl$_5$/Ph$_4$Sn (sample from Table 2, run 3) and WCl$_6$/Ph$_4$Sn (Table 2, run 8), respectively.

This probably stems from the steric hindrance exerted by two phenylethynyl groups existing in close proximity to each other.

*3.4. Structure of poly(**2**)*

The good solubility of poly(**2**)s in common organic solvents allowed structural characterization by various spectroscopic methods. The IR spectra or Mo- and W-based polymers were identical to each other (Fig. 3). The terminal alkyne C–H stretching band observed at 3280–3290 cm^{-1} in monomer **2** was absent in the spectra of the polymers, implying that terminal acetylenic groups underwent complete polymerization. It was difficult to detect the internal C≡C in the monomer and polymer by IR spectroscopy, which should appear between 2100 and 2260 cm^{-1}. This is usual in the case of symmetrically substituted C≡C bonds. As seen in Fig. 4, the ^{13}C NMR spectrum of Mo-based poly(**2**) displayed two resonance peaks at 89 and 93 ppm due to internal C≡C, suggesting that internal triple bonds remained in the polymers, while the peaks at 81 and 82 ppm of terminal C≡C disappeared, which were clearly seen in the spectrum of the monomer. A new broad peak appeared around 140 ppm in the spectrum, which is assignable to the olefinic carbon in the polyene backbone [13]. The ^{1}H NMR spectra showed a very broad peak in the region of 6–8 ppm, which is ascribed to the protons of the aromatic rings (Fig. 5). Similar ^{13}C and ^{1}H NMR spectra were observed in W-based polymers as well.

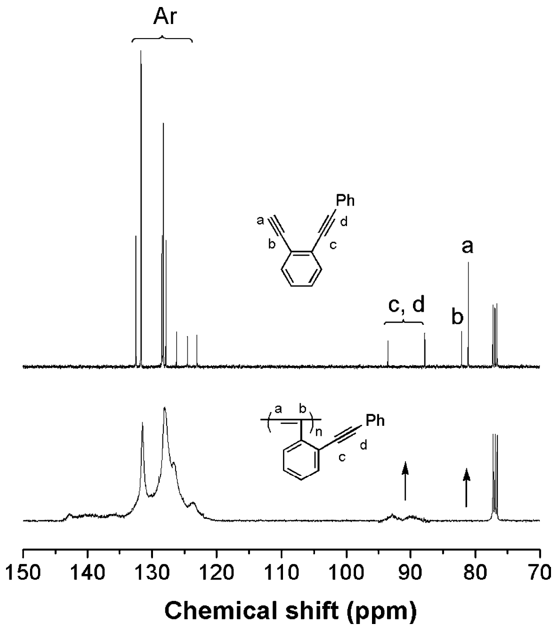


Fig. 4. ^{13}C NMR spectra of monomer **2** and poly(**2**) obtained with MoCl$_5$/Ph$_4$Sn (sample from Table 2, run 3, measured at rt in CDCl$_3$).

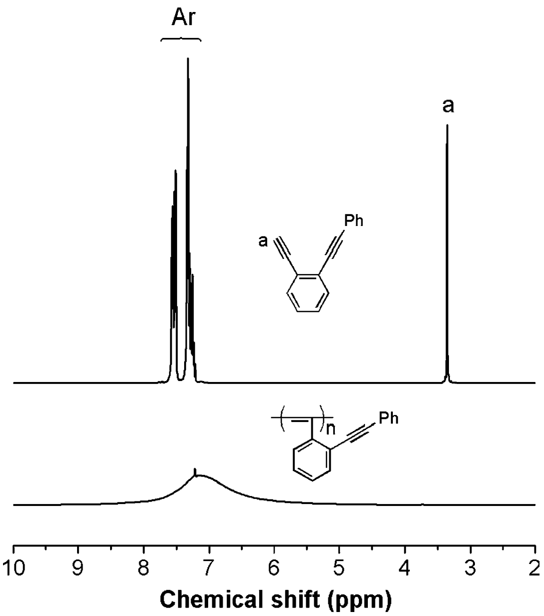


Fig. 5. ^{1}H NMR spectra of monomer **2** and poly(**2**) obtained with MoCl$_5$/Ph$_4$Sn (sample from Table 2, run 3, measured at rt in CDCl$_3$).

The UV–vis spectra of monomer **2** and Mo- and W-based poly(**2**)s are given in Fig. 6. The UV–vis absorptions of the polymers were red-shifted compared to that of the monomer, which are attributed to the conjugation of the main chain. Furthermore, Mo-based poly(**2**) exhibited an absorption maximum at 408 nm, while W-based poly(**2**) showed an absorption shoulder in a shorter wavelength region. This suggests that the former polymer has a longer main-chain conjugation than that of the latter.

The TGA curve of W-based poly(**2**) exhibited a 10% weight loss at 450 °C, while that of Mo-based poly(**2**) showed a 10% weight loss at 300 °C (Fig. 2), suggesting that the former had a higher activation energy of chain scission than the latter. This seems to be associated with the presence of naphthalene-type cyclic moieties (10%) in W-based poly(**2**) according to the result obtained from pyrolysis GC-MS, while they were absent in the Mo-based poly(**2**). Thus, the good thermal stability of the W-based poly(**2**) is attributable to the presence of stronger bonds arising from naphthalene-type cyclic units,

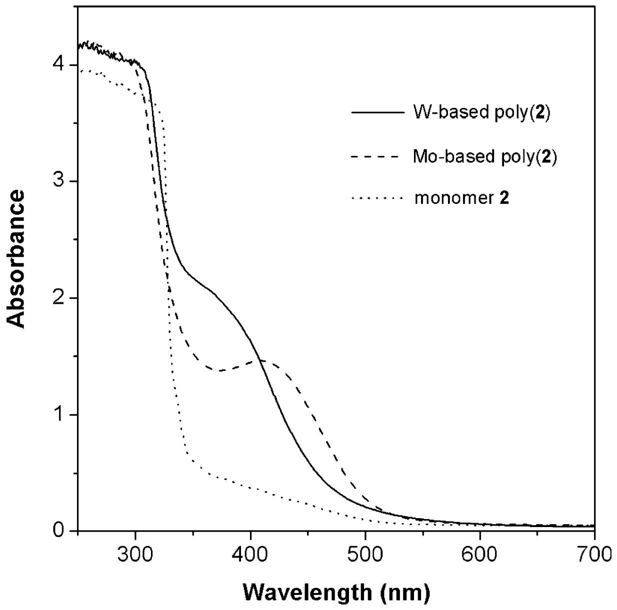
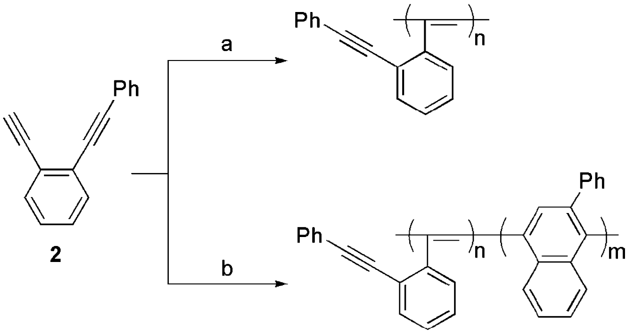


Fig. 6. UV–vis spectra of monomer **2** and poly(**2**)s obtained with $MoCl_5/Ph_4Sn$ (sample from Table 2, run 3) and WCl_6/Ph_4Sn (Table 2, run 8), respectively (measured in THF; solution concentrations: 0.01 mg/mL for monomer **2** and 0.1 mg/mL for poly(**2**)s).



a) $MoCl_5$-based catalyst, in toluene, 60 or 80 °C.
b) WCl_6-based catalyst, in toluene, 60 or 80 °C.

Scheme 3. Polymerization of 1-ethynyl-2-phenylethynylbenzene (**2**).

which was formed by the head-to-head intramolecular cyclization between the adjacent terminal and internal triple bond. Therefore, the Mo-based poly(**2**) structure should possess the structure of poly(phenylacetylene) main chain with unreacted phenylacetylene group (route a, Scheme 3), whereas the W-based poly(**2**) contains two types of segments, the major part is poly(phenylacetylene) main chain with unreacted phenylacetylene group and the minor part is naphthalene-type cyclic units (route b, Scheme 3).

4. Conclusions

Poly(*o*-diethynylbenzene)s with different structures were obtained with various transition metal catalysts. The Rh-based catalyst polymerized one of the two ethynyl groups into poly(phenylacetylene) chain and around 70% of the second ethynyl group remained intact. Diene and methylenediene units were observed in pyrolysis GC-MS analysis, which suggests that the five-membered ring in the polymer was formed by head-to-tail cyclization between the two adjacent ethynyl groups. In contrast to Rh-based catalysts, the Ta-based catalysts completely consumed both of the ethynyl groups to form cross-linked polymer mainly consisting of trisubstituted benzene rings, in high yield. The benzene-predominant structure was formed by the intermolecular cyclotrimerization of the monomer. Additionally, 1-ethynyl-2-phenylethynylbenzene, one of *o*-diethynylbenzene derivatives, was successfully polymerized by W and Mo catalysts to yield soluble polymers with M_n of 6300–71,900. Although the W- and Mo-based polymers possessed similar structures, mainly composed of a poly(phenylacetylene) main chain, a naphthalene-type cyclic unit was also formed by head-to-tail cyclization between the terminal and internal adjacent triple bonds in the W-based polymer.

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