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Synthesis and Properties of a Novel Polyacetylene Containing Eugenol Moieties

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ABSTRACT

This work deals with the synthesis of a novel polyacetylene containing eugenol moieties, and characterization of the general properties of the formed polymer. The polymerization of 4-allyl-2-methoxy-1-prop-2-ynyloxybenzene (**1**) with $[(\mathrm{nbd})\mathrm{RhCl}]_2$ and $(\mathrm{nbd})\mathrm{Rh}^+[\eta^6\text{-}\mathrm{C_6H_5B^-(C_6H_5)_3}]$ catalysts gave the polymer [poly(**1**)] with number-average molecular weights ranging from 12,100 to 31,400 in good yields. With $\mathrm{MoCl_5}$ as a catalyst, poly(**1**) was obtained in a poor yield. Employment of n-$\mathrm{Bu_4Sn}$ as a cocatalyst was effective to increase the polymer yield. W catalysts were not effective to the polymerization of **1**. Poly(**1**) was soluble in common organic solvents, film-forming, and thermally stable up to 150°C. Poly(**1**) exhibited the UV-VIS absorption maxima at 280 nm, and broad absorption assignable to a conjugated polyacetylene main chain at 300–450 nm.

Key Words: Eugenol; Polyacetylene; Rh catalyst; Mo catalyst.

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INTRODUCTION

Eugenol (4-allyl-2-methoxyphenol) is a main component (80 wt%) of clove oil, which is mainly produced in Indonesia. It is widely used as perfumes, antioxidants, drugs, foods, and taste items.[1,2] Eugenol is an inexpensive natural resource, which carries reactive phenolic hydroxyl and allyl groups, and is therefore expected as a key component for environmentally friendly organic synthetic chemistry. Several researchers have also attempted to utilize eugenol in polymer synthetic chemistry. Ciszewsky and Milczarek have synthesized polyeugenol by electropolymerization, and examined it as chemo- and biosensors.[3–5] Bailly et al.[6] have synthesized bisphenol-A polycarbonate/eugenol-siloxane copolymers. Peppas et al.[7] have studied the incorporation and release of eugenol from glassy hydrophilic copolymers. Mata et al.[8] have synthesized dendrimers utilizing hydrosilylation of the double bond of eugenol. Tappe et al.[9] have examined the scope and limitations of sharpless asymmetric dihydroxylation of polymer-bound olefins including eugenol. On the other hand, polyacetylene and its derivatives are interesting, because polyacetylenes possess alternating double bonds in the main chain, which endow them with electrical conductivity, chemical reactivity, and gas permeability. These backgrounds stimulated the authors to study the polymerization of substituted acetylene having eugenol, an environmentally friendly inexpensive natural resource. This work deals with the synthesis of a novel polyacetylene containing eugenol moieties and the examination of general properties of the formed polymer.

EXPERIMENTAL

Measurements

IR, UV-VIS, and NMR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer, a Shimadzu UV-2200 spectrophotometer, and a JOEL EX-400 spectrometer, respectively. Thermogravimetric analysis (TGA) was conducted on a Perkin Elmer TGA7 thermal analyzer at a heating rate of 10°C/min in air. Number- and weight-average molecular weights (M_n and M_w, respectively) were estimated by GPC with Shodex K804, K805, and K806 columns eluted with THF as an eluent, a polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors. Elemental analysis was carried out at the Kyoto University Elemental Analysis Center.

Materials

Eugenol (purity 99.99%) was obtained from Indeso Co. All the reagents in monomer synthesis were used as purchased without purification. Solvents used for polymerization were purified before use by the standard procedures. (nbd)$Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ (nbd = 2,5-norbornadiene) was prepared by the reaction of $[(nbd)RhCl]_2$ with $NaB(C_6H_5)_4$ as described in the literature.[10] $[(nbd)RhCl]_2$ was obtained from Aldrich and used as received. WCl_6, WCl_4 and $MoCl_5$ were obtained from Wako and used as received.

Synthesis of 4-Allyl-2-methoxy-1-prop-2-ynyloxybenzene (1)

Potassium carbonate (23.18 g, 0.17 mol) was added to a solution of eugenol (55.27 g, 0.34 mol) in ethanol (200 ml). After the reaction mixture was stirred at room temperature for 1 h, propargyl chloride (25 g, 0.34 mol) was added drop wise to the mixture. The resulting mixture was heated with refluxing overnight. Ether was added to the mixture, and the organic phase was washed with water. The organic phase was dried over $MgSO_4$. After the removal of the solvent with a rotary evaporator, the residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 5/1, volume ratio) to obtain a colorless oil in 54% yield; 1H NMR (400 MHz, $CDCl_3$): δ 2.49 (*s*, 1H, $\equiv CH$), 3.34 (*d*, $J = 8.5$ Hz, 2H, $CH_2{-}CH{=}CH_2$), 3.85 (*s*, 3H, CH_3), 4.74 (*s*, 2H, $O{-}CH_2{-}$), 5.08 (*d*, $J = 8.0$ Hz, 2H, $=CH_2$), 5.94–6.07 (*m*, 1H, $-CH=$), 6.72–6.97 (*m*, 3H, Ar), ^{13}C NMR (400 MHz, $CDCl_3$): δ 39.8 ($\underline{C}H_2CH{=}CH_2$), 55.7 ($OCH_3$), 56.8 ($\underline{C}H_2CHCH$), 75.6, 78.7 (CCH), 112.1, 114.4, 120.2 (C_6H_3), 115.7 (CH_2CHCH_2), 134.1 (C_{ipso} bounded to CH_2), 137.4 (CCH_2), 144.9 (C_{ipso} bounded to $-OCH_2$), 149.5, (C_{ipso} bounded to $-OCH_3$), IR (NaCl, neat): 3300 ($\nu_{\equiv CH}$), 3001, 2831, 2150 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=C}$), 1589 cm^{-1}. Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.24; H, 6.99.

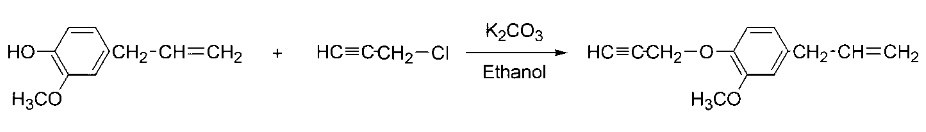
Polymerization

A solution of **1** (0.404 g, 2 mmol) and a catalyst in a solvent (2 mL) was kept for 24 h in a glass tube under nitrogen. The resulting solution was diluted with toluene (0.5 mL) and then poured into hexane (600 mL) to precipitate a polymer. Filtration followed by drying under reduced pressure gave filmy poly(**1**).

RESULTS AND DISCUSSION

Monomer Synthesis

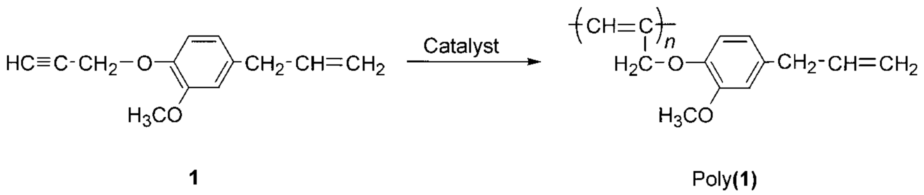
The novel monomer, **1** was synthesized from eugenol and propargyl chloride in the presence of potassium carbonate in ethanol as a solvent in 54% yield (Sch. 1). The structure of **1** was confirmed by ^1H-, ^{13}C-NMR, and IR spectroscopies, beside elemental analysis.



Eugenol

1

Scheme 1. Synthesis of monomer **1**.



1 Poly(**1**)

Scheme 2. Polymerization of monomer **1**.

Polymerization

The polymerization of **1** was conducted in THF, CH_2Cl_2 and toluene with Rh, Mo, and W catalysts (Sch. 2), which are effective for the polymerization of monosubstituted acetylenes,[11–13] and the results are summarized in Table 1. **1** satisfactorily polymerized with $[(nbd)RhCl]_2$ and $(nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ catalysts to give yellow-brown polymers with M_n ranging from 12,100 to 31,400 quantitatively (Table 1, runs 1–6) in THF and CH_2Cl_2. $[(nbd)RhCl]_2$ afforded the polymers with larger M_n and smaller polydispersity index than $(nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ did, although the differences were small. Use of Et_3N in the polymerization of **1** with $[(nbd)RhCl]_2$ reduced the M_n and polydispersity index of the polymer (runs 2 and 4). This result differs from the general trend, i.e., the polymerization of phenylacetylenes with $[(nbd)RhCl]_2$ alone gives the polymers in poor yields, while employment of Et_3N is effective to increase the yield and M_n.[14–17] At present, the reason for this finding is not clear. The polymerization of **1** with $MoCl_5$ also gave the polymer with M_n of 31,700 (run 7), but the yield was low (25%). Use

Table 1. Polymerization of **1** with various transition-metal catalysts.[a]

				Polymer[b]		
Run	Catalyst	Solvent	Temperature (°C)	Yield (%)	$M_n{}^c \times 10^{-3}$	$M_w/M_n{}^c$
1	$[(nbd)RhCl]_2$	THF	30	99	31.4	1.9
2	$[(nbd)RhCl]_2$—Et_3N	THF	30	99	31.0	1.4
3	$[(nbd)RhCl]_2$	CH_2Cl_2	30	99	29.8	1.8
4	$[(nbd)RhCl]_2$—Et_3N	CH_2Cl_2	30	99	12.1	1.6
5	$(nbd)Rh^+ [\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$	THF	30	99	22.6	2.0
6	$(nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$	CH_2Cl_2	30	99	26.6	2.4
7	$MoCl_5$	Toluene	80	25	31.7	1.9
8	$MoCl_5$–n-Bu_4Sn	Toluene	30	99	13.9	1.4
9	WCl_6	Toluene	80	8	4.7	3.0
10	WCl_6–n-Bu_4Sn	Toluene	30	Trace	—	—
11	WCl_4	Toluene	80	Trace	—	—
12	WCl_4–n-Bu_4Sn	Toluene	30	Trace	—	—

[a] Polymerization conditions: $[M]_0 = 2.0\,M$, $[Cat] = 10\,mM$, $[Cocat]/[Cat] = 2$, for 24 h.
[b] n-Hexane-insoluble part.
[c] Determined by GPC (THF elution, PSt standard).

of n-Bu_4Sn as a cocatalyst (run 8) resulted in the increase of polymer yield (99%) and the decrease of M_n (13,900). On the other hand, polymerization with W catalysts yielded only a trace amount of polymer with low M_n even in the presence of n-Bu_4Sn (runs 9–12).

Structure of the Polymer

The structure of poly(**1**) obtained with $[(nbd)RhCl]_2$ catalyst (run 1 in Table 1) was examined by IR and ^1H NMR spectroscopies. In the IR spectrum of **1**, the stretching vibration peaks of $\equiv$C–H and C$\equiv$C were clearly detected at 3300 and 2150 cm^{-1}, respectively (Fig. 1). In the spectrum of poly(**1**), these peaks completely disappeared, which indicates the proceeding of acetylene polymerization as expected. On the other hand, the stretching vibration peak of C=C at 1637 cm^{-1} was observed both in the IR spectra of **1** and poly(**1**), which confirms that the allyl group of **1** was intact during the polymerization.

Figure 2 depicts the ^1H NMR spectra of **1** and poly(**1**). The latter clearly exhibited the signals assignable to a polyacetylene having the eugenol moiety in the side chain. These IR and ^1H NMR spectroscopic data confirm that the polymerization took place at

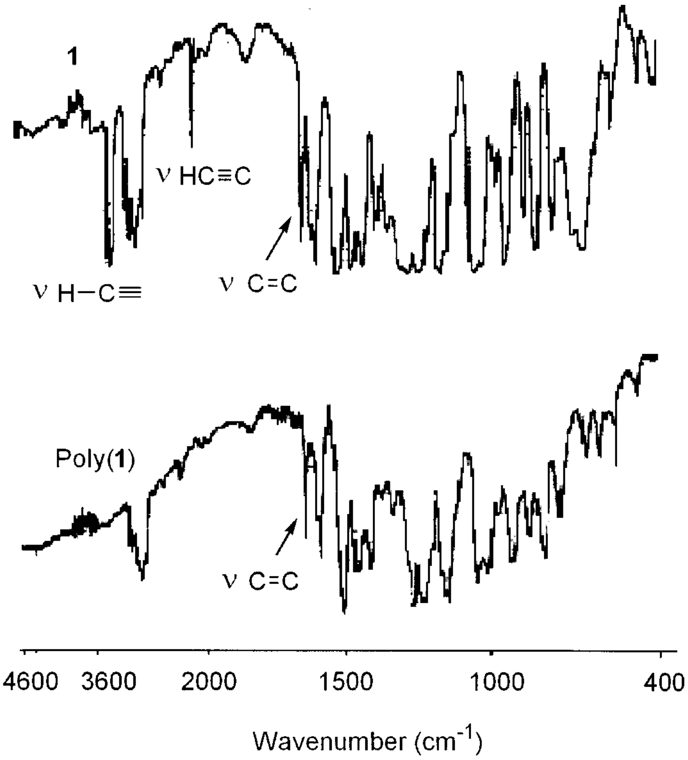


Figure 1. IR spectra of **1** and poly(**1**) (sample: run 1 in Table 1).

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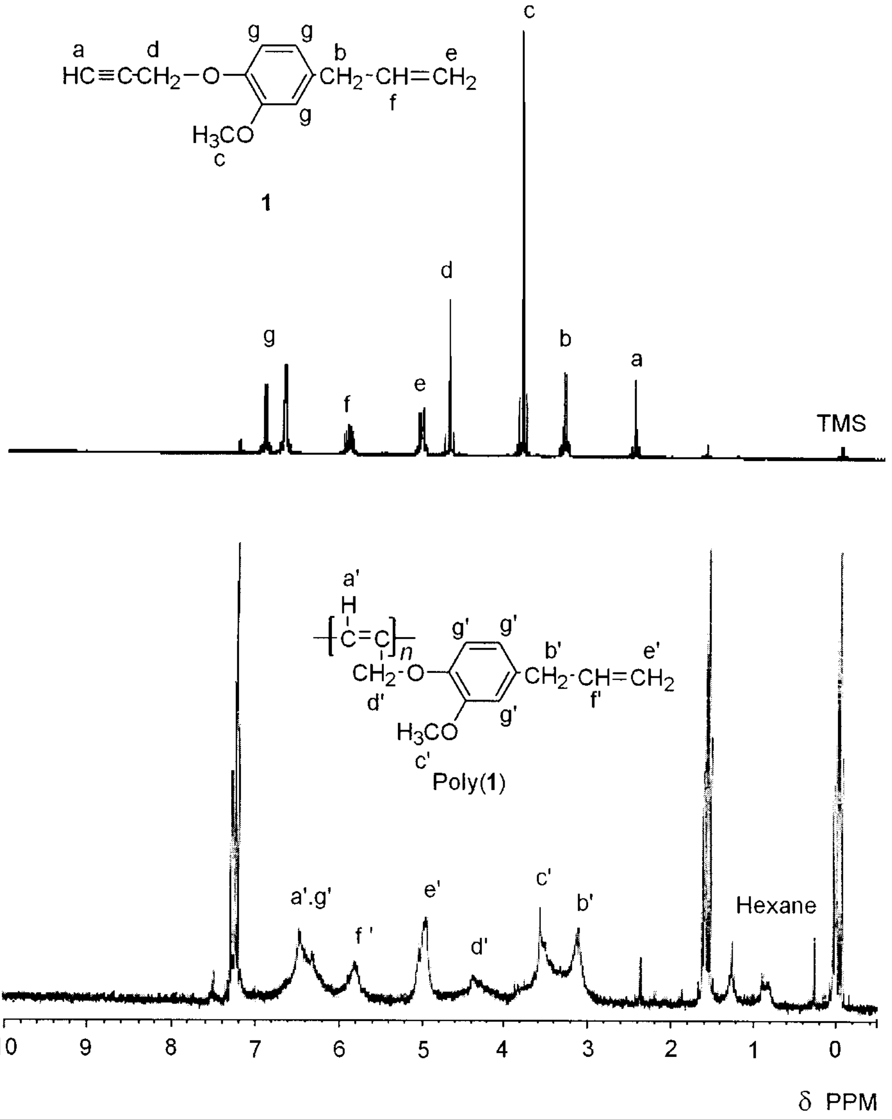

Figure 2. ^{1}H NMR spectra of **1** and poly(**1**) (sample: run 1 in Table 1) measured in $CDCl_3$.

the triple bond of **1** to afford the polymer with alternating double bonds in the main chain and eugenol in the side chain. It has been reported that Rh catalysts give a polyacetylene derivative, which shows ^{1}H NMR sharp signal based on the cis olefinic proton in the main chain around 6–7 ppm.[14–17] The resulting poly(**1**), however, showed broad olefinic and aromatic proton signals in this region. It was impossible to decide the geometrical structure of the main chain. The polymers obtained by Mo-catalyzed polymerization showed almost the same ^{1}H NMR spectroscopic patterns as for the Rh-based polymer.

Polymer Properties

Poly(**1**) was totally soluble in benzene, THF, toluene, chloroform, DMF, acetone, and DMSO, partially soluble in ether and methanol, but insoluble in hexane and water. Poly(**1**) exhibited UV-VIS absorption maxima at 280 nm (Fig. 3), which were nearly the same as for the monomer. Broad absorptions at 300–450 nm are characteristic of conjugated double bonds. The UV-VIS absorption of poly(**1**) prepared with $MoCl_5$ catalyst was broader than those of Rh-based of poly(**1**)s, and the absorption of the polymer prepared with $(nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ catalyst was less broad than that with $[(nbd)RhCl]_2$. This indicates that the extent of conjugation of the double bonds of poly(**1**) is the following order, $MoCl_5 > [(nbd)RhCl]_2 > (nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$, which agrees with the order of M_n.

Poly(**1**) gradually lost the weight above 150°C under air (Fig. 4). The gradual weight loss bellow 300°C is presumably due to the cleavage of the methoxy and allyl groups from the polymer. A sharp weight loss was observed above 375°C, suggesting the beginning of main chain fission at this temperature.

CONCLUSION

In this paper, we demonstrated the polymerization of a novel eugenol-derived propargyl ether (1) with insertion and metathesis catalysts, and determined the structure and general properties of the formed polymer. $[(nbd)RhCl]_2$, $(nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ and $MoCl_5$–n-Bu_4Sn catalysts were very effective to the polymerization of 1, while W catalysts were not. The allyl group was intact during the acetylene polymerization, and the polymer was soluble in common organic solvents including THF, benzene, toluene,

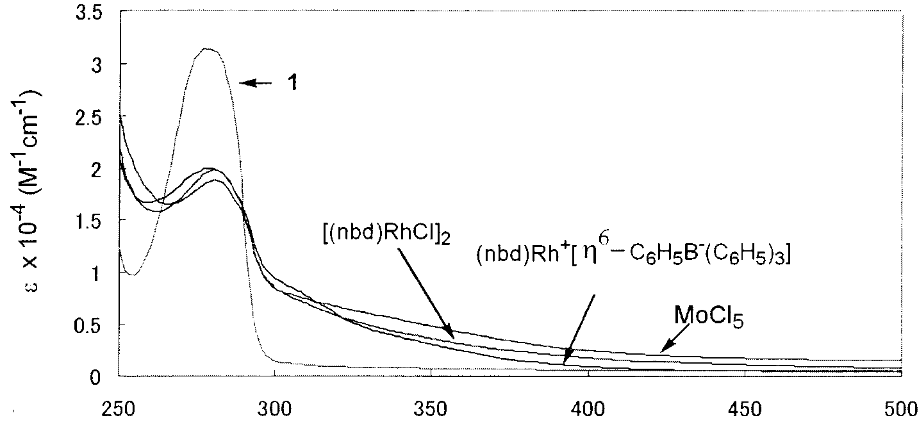

Figure 3. UV-*vis* spectra of **1** and poly(**1**) (sample: runs 1, 3 and 5 in Table 1) measured in THF (concentration 1.0×10^{-4} mol/L).

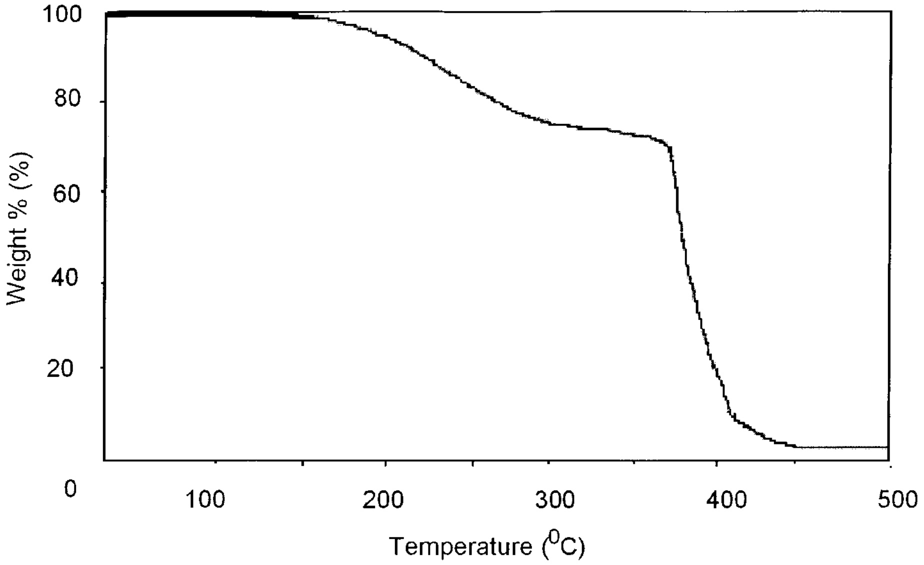

Figure 4. TGA curve of poly(**1**) (sample: run 1 in Table 1) measured under air with a heating rate of 10°C/min.

CH_2Cl_2 chloroform, DMF, acetone, and DMSO. The polymer exhibited the UV-VIS absorption maxima at 280 nm, and broad absorption assignable to a conjugated polyacetylene main chain at 300–450 nm. It was thermally stable up to 150°C under air.

Eugenol, an inexpensive natural product carrying reactive phenolic hydroxyl and allyl groups seems to be a candidate of a key component in environmentally friendly organic and polymer synthetic chemistry. Further research on the synthesis of novel polymers from eugenol as a starting material is in progress.

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