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Synthesis and Properties of Novel Eugenol-Based Polymers

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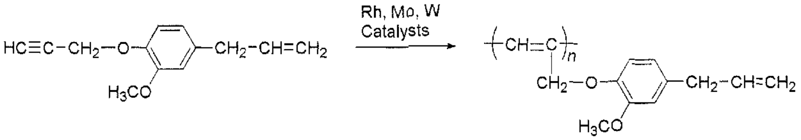
Summary

This work deals with the synthesis and characterization of novel eugenol-based polymers. The polymerization of 2-methoxy-4-propenyl-1-prop-2-ynyloxybenzene (**1**) with Rh, Mo, and W catalysts gave the corresponding polyacetylene [poly(**1**)], while that using BF_3 catalyst gave poly(**1**)′, without affecting the triple bond. A novel cross-linked polyacetylene was synthesized from poly (**1**)′ with $[(nbd)RhCl]_2$–Et_3N catalyst.

Introduction

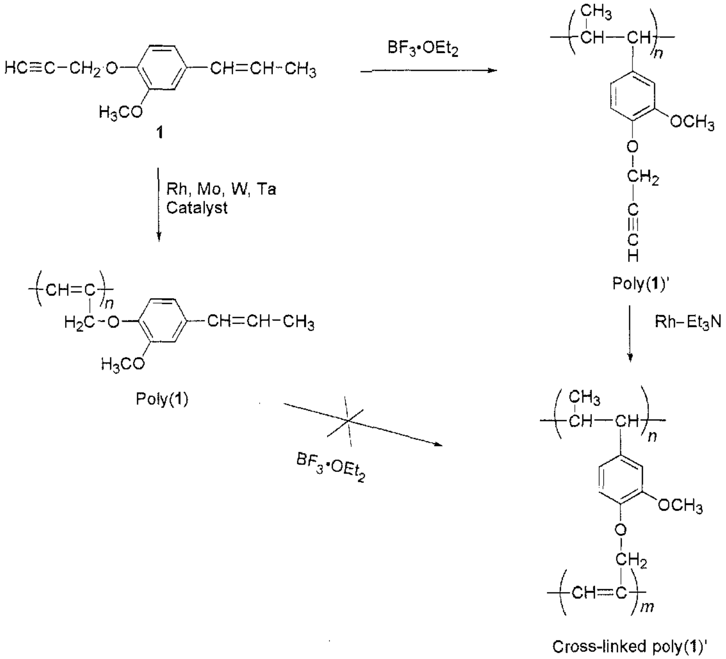
Eugenol (4-allyl-2-methoxyphenol) is a main component (80 wt%) of clove oil, which is mainly produced in Indonesia. It is widely used as perfumes, antioxidants, drugs, foods, and taste items [1–2]. Several researchers have attempted to utilize eugenol in synthetic polymer chemistry. For instance, Ciszewsky and Milczarek have synthesized polyeugenol by electropolymerization, and examined it as chemo- and biosensors [3–5]. Bailly et al. have synthesized bisphenol-A polycarbonate/eugenol-siloxane copolymers [6]. Peppas et al. have studied the incorporation and release of eugenol from glassy hydrophilic copolymers [7]. Mata et al. have synthesized dendrimers utilizing hydrosilylation of the double bond of eugenol [8]. Tappe et al. have examined the scope and limitations of Sharpless asymmetric dihydroxylation for polymer-bound olefins of different structural types including eugenol [9]. 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.

The authors recently reported the synthesis and polymerization of novel eugenol-based monomer, 4-allyl-2-methoxy-1-prop-2-ynyloxybenzene with Rh, Mo, and W catalysts (Scheme 1) [10]. The corresponding polyacetylene with moderate molecular weights was obtained in good yields, wherein the allyl group was intact during the polymerization. If we prepare the analogous monomer with 1-propenyl group instead of allyl group, we can expect cationic polymerization at the 1-propenyl group apart from acetylene polymerization at the propynyl group.



Scheme 1. Polymerization of 4-allyl-2-methoxy-1-prop-2-ynyloxybenzene with Rh, Mo, and W catalysts

The present work deals with the synthesis and polymerization of a novel eugenol-based monomer having double and triple bonds, and the examination of general properties of the formed polymer (Scheme 2).



Scheme 2. Polymerization of a novel eugenol-based monomer having double and triple bonds

Experimental

Materials

Isoeugenol [2-methoxy-4-(1-propenyl) phenol] was obtained from Tokyo Kasei Kogyo Co., LTD. 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 [11]. $[(nbd)RhCl]_2$ was obtained from Aldrich and used as received. WCl_6, WCl_4 and $MoCl_5$ were obtained from Wako and used as received.

Instruments

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) were estimated by GPC with Shodex K804, K805, and K806 columns eluted with THF as an eluent, polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors. Elemental analysis was carried out at the Kyoto University Elemental Analysis Center.

*Synthesis of 2-Methoxy-4-propenyl-1-prop-2-ynyloxybenzene (**1**)*

Potassium carbonate (23.18 g, 0.17 mol) was added to a solution of isoeugenol (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 dropwise 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, then 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 white solid in 51% yield; mp 40–43 °C. ^1H NMR (400 MHz, $CDCl_3$) : δ 1.59-1.91 (m, 3H, CH_3), 2.49 (s, 1H, $\equiv CH$), 3.89 (s, 3H, OCH_3), 4.74 (s, 2H, $O\text{-}CH_2$), 6.08-6.14 (m, 1H, $=C\underline{H}\text{-}CH_3$), 6.32-6.35 (m, 1H, -CH=), 6.84-7.01 (m, 3H, Ar). ^{13}C NMR (400 MHz, $CDCl_3$): δ 15.5 ($\underline{C}H_3CH{=}CH$), 55.7 (OCH_3), 56.8 (CH_2), 75.6, 78.7 ($C\equiv CH$), 112.1, 114.4, 120.2 (C_6H_3), 115.7 ($CHCHCH_3$), 130.1 (C_{ipso} bonded to CH), 130.4 (CCH), 144.9 (C_{ipso} bonded to $-OCH_2$), 149.5, (C_{ipso} bonded to $-OCH_3$). IR (KBr): 3252.4 ($\nu_{\equiv CH}$), 3001, 2831, 2131 ($\nu_{C\equiv C}$), 1601 ($\nu_{C=C}$), 1583 cm^{-1}. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found : C, 77.16; H, 6.94.

Polymerization

Polymerization with Transition Metal Catalysts

A solution of **1** (0.404 g, 2 mmol) and a catalyst in a solvent (2 ml) was kept at 30 °C for 24 h in a glass tube under nitrogen. The reaction mixture 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 yellow powdery poly(**1**).

Polymerization with $BF_3{\bullet}OEt_2$

A solution of **1** (0.60 g, 3.0 mmol) and $BF_3{\bullet}OEt_2$ (3 µL , 0.03 mmol) in a solvent (4.0 mL) was kept in a glass tube at -78 °C under nitrogen. The resulting solution was poured into hexane (600 mL) to precipitate a polymer. Filtration followed by drying under reduced pressure gave red–violet filmy poly(**1**)′.

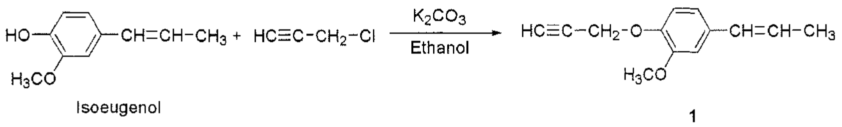
*Cross-linking of Poly(**1**) and Poly(**1**)′*

A solution of a polymer and a catalyst in a solvent was kept in a glass tube at 30 °C for 1 h under nitrogen. The resulting solution was poured into a large amount of methanol to precipitate a polymer. Filtration followed by drying under reduced pressure gave a cross-linked polymer.

Results and discussion

Monomer Synthesis

The novel monomer, **1** was synthesized from isoeugenol and propargyl chloride in the presence of potassium carbonate in ethanol as a solvent in 51% yield (Scheme 3). The structure of **1** was confirmed by ^{1}H-, ^{13}C-NMR, and IR spectroscopies, besides elemental analysis.



Scheme 3. Synthesis of monomer **1**

Polymerization

The polymerization of **1** was conducted in THF, CH_2Cl_2 and toluene with Rh, Mo, W, and Ta catalysts (Scheme 2), which are effective in the polymerization of mono- or disubstituted acetylenes, [12,13] and the results are summarized in Table 1. The polymerization of **1** with $[Rh(nbd)Cl]_2$ alone gave the polymer in 56–70% with M_n 34,800–38,400 (Table 1; runs 1 and 3). Using Et_3N as a cocatalyst increased the yield and polydispersity but decreaced the M_n (runs 2 and 4). This result was the same as general trend i.e., the polymerization of phenylacetylene derivatives with Rh alone proceeds in various solvents to give the polymers in poor yields, while employment of Et_3N is effective to increase the yields [14, 15]. The polymerization of **1** with $MoCl_5$–*n*-Bu_4Sn also gave the polymer with M_n of 14,000 (run 6) in a good yield. On the other hand, polymerization with W yielded only a small amount of oligomers (run 7). It is not clear why the W-based catalyst was not active to the relevant monomer. The authors suppose that cyclic trimers were formed due to lack of crowdedness at the triple bond as previously reported. No hexane-insoluble product was formed in the polymerization with Ta catalyst (runs 8 and 9).

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

Run	Catalyst	Solvent	Yield[b] (%)	M_n[c] x 10^{-3}	M_w/M_n[c]
1	$[(nbd)RhCl]_2$	THF	70	38.4	1.6
2	$[(nbd)RhCl]_2$–Et_3N	THF	100	30.7	1.9
3	$[(nbd)RhCl]_2$	CH_2Cl_2	56	34.8	1.5
4	$[(nbd)RhCl]_2$–Et_3N	CH_2Cl_2	100	29.2	1.8
5	$(nbd)Rh^{+}[\eta^6\text{-}C_6H_5B^{-}(C_6H_5)_3]$	THF	100	27.3	2.4
6	$MoCl_5$–*n*-Bu_4Sn	Toluene	94	14.0	1.8
7	WCl_6–*n*-Bu_4Sn	Toluene	10	0.9	1.7
8	$TaCl_5$	Toluene	-	-	-
9	$TaCl_5$–*n*-Bu_4Sn	Toluene	-	-	-

a) Polymerization conditions ; $[M]_0$ = 2.0 M, [Cat] = 10 mM , [Cocat]/[Cat] = 2, 30 °C, 24 h.
b) *n*-Hexane-insoluble part. c) Determined by GPC (THF elution, PSt standard).

Table 2 summarizes the polymerization of **1** with $BF_3{\bullet}OEt_2$ as a catalyst. Filmy polymers with M_n of 500–1,200 were obtained in 25–95% yields. The yield and M_n

of the polymer tended to increase as lowering the polymerization temperature in toluene. In CH_2Cl_2, the polymerization at –60 °C for 1 h afforded the polymer with higher M_n and yield than that at –78 °C for 24 h.

Table 2. Polymerization of **1** with $BF_3 \cdot OEt_2$ catalyst[a]

Run	Temperature (°C)	Solvent	Time (h)	Yield[b] (%)	$M_n^c \times 10^{-3}$	M_w/M_n^c
1	-78	Toluene	24	43	1.2	1.0
2	-60	Toluene	24	25	0.6	1.5
3	30	Toluene	24	25	0.5	1.3
4	-78	CH_2Cl_2	24	25	0.5	1.1
5	-60	CH_2Cl_2	1	95	1.2	1.3

a) Polymerization conditions; $[M]_0 = 0.75$ M, [Cat] = 7.5 mM.

b) *n*-Hexane-insoluble part. c) Determined by GPC (THF elution, PSt standard).

Cross-linking of poly(**1**)′ was carried out with Rh–Et_3N catalyst. Cross-linking of poly(**1**)′ in THF gave a solvent-soluble product, while that in toluene afforded a solvent-insoluble polymer.

Table 3. Cross-linking of poly(**1**) ′ [a]

Run	$[M]_0$ (mol/L)	Solvent	Yield[b] (%)	$M_w^c \times 10^{-3}$	M_w/M_n^c	Solubility[d]
1	2.0	THF	99	15.0	11.6	O
2	0.2	Toluene	87	nd[e]	nd[e]	×

a) Polymerization conditions; $[M]_0$/[Cat] = 100, [Cocat]/[Cat] = 2, 30 °C, 1 h.

b) Methanol-insoluble part. c) Determined by GPC (THF elution, PSt standard).

d) O = Soluble. × = Insoluble. e) Not determined due to insolubility of the product.

Structure of the Polymers

The structure of poly(**1**) obtained with $[(nbd)RhCl]_2$–Et_3N catalyst (run 2 in Table 1) was examined by IR and ^{1}H 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 (Figure 1). In that 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 double bond of **1** was intact during the polymerization. Figure 2 depicts the ^{1}H-NMR spectra of **1** and poly(**1**). The latter clearly exhibited the signals assignable to a polyacetylene having isoeugenol moiety in the side chain. From these IR and ^{1}H-NMR spectroscopic data, it is confirmed that the polymerization took place at the triple bond of **1** to afford the polymer with alternating double bonds in the main chain and isoeugenol in the side chain.

The IR and ^{1}H-NMR spectra of poly(**1**)′ are also shown in Figures 1 and 2. It is clear from the disappearance of the resonance peak at 6.0–6.5 ppm in the ^{1}H-NMR spectrum that the double bond is absent in poly(**1**)′. The methyl proton signal shifted from 1.8 (connected to *sp*^{2} carbon) to 1.0 ppm (connected to *sp*^{3} carbon). The presence of -C$\equiv$C-H was confirmed by the IR absorption peak at 3300 cm^{-1} and

2150 cm^{-1} and the $-C{\equiv}C-H$ proton signal at 2.3 ppm in the ^1H-NMR spectrum. From the IR and NMR spectra of poly(**1**)′, it is confirmed that the polymerization took place at the double bond of **1** and the triple bond was intact during the polymerization.

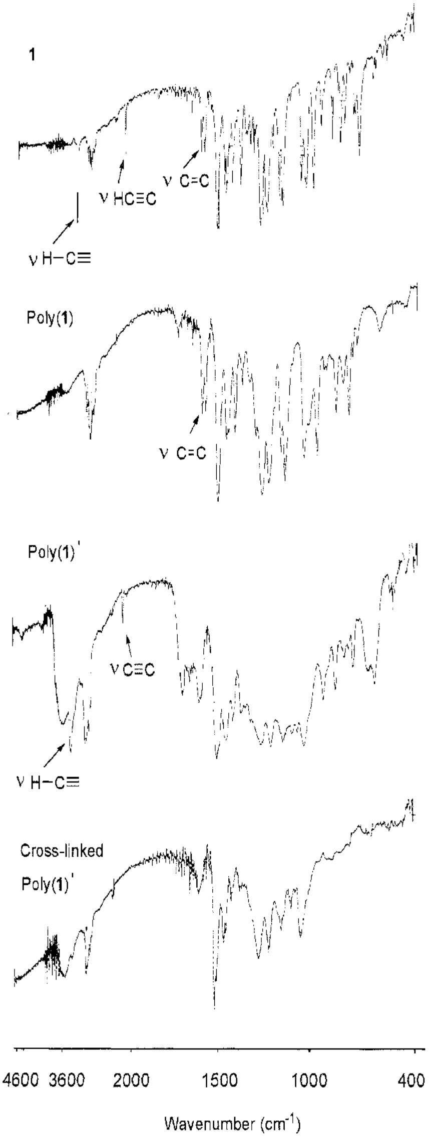


Figure 1. IR spectra of **1**, poly(**1**), poly(**1**)′ and cross-linked poly(**1**)′.

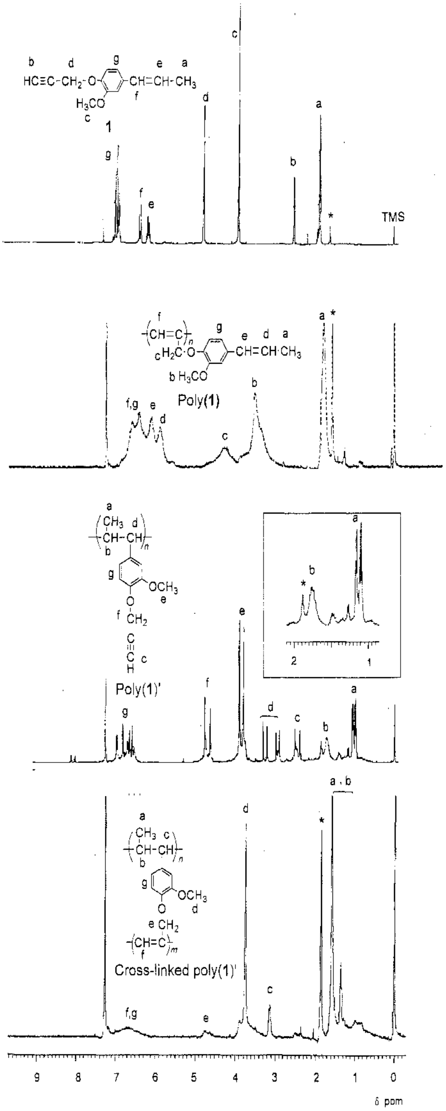


Figure 2. ^1H-NMR spectra of **1**, poly(**1**), poly(**1**)′ and cross-linked poly(**1**)′. $*$: H_2O.

The conversion of the triple bond by treatment of poly(**1**)′ with Rh catalyst was confirmed by the IR (Figure 1) and the ^{1}H-NMR spectra (Figure 2). The solvent-soluble cross-linked poly(**1**)′ exhibited a very broad GPC profile. On the other hand, cross-linking of poly(**1**) with $BF_3 \bullet OEt_2$ was unsatisfactory. No solvent-insoluble product was obtained, and the GPC trace of the recovered polymer exhibited a multimodal peak at the region of rather lower molecular weights than that of poly(**1**). It is assumed that degradation of the polyacetylene main chain was caused by the catalyst.

Polymer Properties

As shown in Figure 3, poly(**1**) exhibited the UV-vis absorption maximum at 262 nm, which was 4 nm longer than that of the monomer. The broad absorption at 300–450 nm is characteristic of conjugated double bonds. On the other hand, poly(**1**)′ did not exhibit this broad absorbtion, which supports the absence of polyacetylene structure. The UV-vis spectrum of cross-linked poly(**1**)′ also showed broad absorption at 300–450 nm, but the intensity was weak. The conjugation length may be shorter than that of poly(**1**), presumably due to the low efficiency of cross-linking. The UV-vis absorption maximum of poly(**1**) appeared at longer wavelength region compared with that of cross-linked poly(**1**)′. It is likely that the polymerization degree of cross-linked poly(**1**)′ was lower than that of poly(**1**).

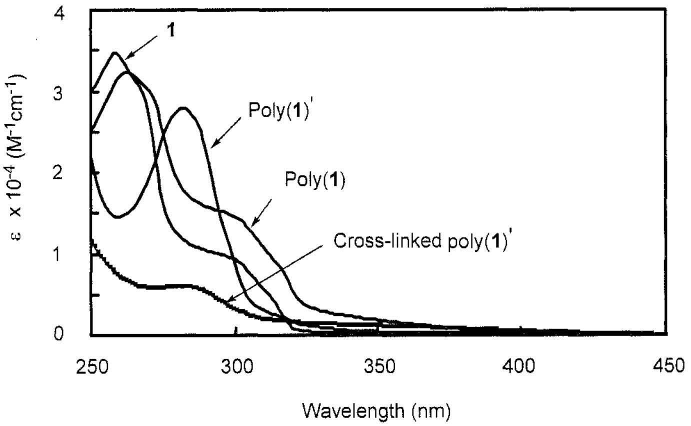


Figure 3. UV-vis spectra of **1**, poly(**1**), poly(**1**)′ and cross-linked poly(**1**)′ measured in THF (concentration 1.0 x 10^{-4} mol/L).

Poly(**1**), poly(**1**)′ and cross-linked poly(**1**) and poly(**1**)′ (except run 2 in Table 3) were totally soluble in benzene, THF, toluene, chloroform, DMF, acetone, and DMSO, partly soluble in ether and methanol, but insoluble in hexane and water. Poly(**1**) gradually lost weight above 150 °C under air, while cross-linked poly(**1**)′ did above 250 °C. It is assumed that cross-linking is effective to enhance the thermal stability of the polymer.

Conclusions

In this paper, we have studied the polymerization of novel eugenol-based propargyl ether (**1**) with insertion, metathesis and cationic catalysts, and revealed 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 effective to the polymerization of **1**. The 1-propenyl group was intact during the acetylene polymerization. On the other hand, polymerization of **1** with $BF_3 \cdot OEt_2$ gave poly(**1**)′ keeping the triple bond intact. Cross-linked polymers could be obtained from poly(**1**)′ with Rh catalyst. Cross-linking of poly(**1**) with $BF_3 \cdot OEt_2$ was unsatisfactory due to degradation of the polyacetylene main chain.

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