

Synthesis of Soluble Novel Polyacetylenes Containing Carbamate and Eugenol Moieties

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Abstract: This study was aimed to synthesize a series of novel polyacetylenes containing carbamate and eugenol moieties. The polymerization of 1-(3,4-dimethoxyphenyl)propane-2-yl prop-2-ynylcarbamate (1), 1-(3,4-dimethoxyphenyl)propane-2-yl 3-ethynyl phenylcarbamate (2), 1-(3,4-dimethoxyphenyl)propane-2-yl 4-ethynylphenylcarbamate (3), (2S)-1-(3,4-dimethoxyphenyl)propane-2-yl 2-((prop-2ynoxy)carbonylamino)propanoate (4) in the presence of (nbd)Rh⁺[η⁶-C₆H₅B(C₆H₅)₃] as catalyst have successfully produced corresponding polyacetylenes [poly(1)–poly(4)] in high yield. The molecular weight of the synthesized polyacetylenes ranged between 13,900–18,400 g/mol. In particular, the molecular weight of poly(1) could be increased by the addition of menthol. Practically, these polymers were found to have a stable helical structure and soluble in common organic solvents.

Keywords: polyacetylenes; carbamate; eugenol; Rh catalyst; helical structure

■ INTRODUCTION

Eugenol (4-allyl-2-methoxyphenol) has been recognized to approximately covering 80–90% of the clove oil weight. In fact, it is primarily produced and continued to grow in Indonesia [1-2]. In general, the eugenol compound has the molecular formula of C₁₀H₁₂O₂, which contains several functional groups, including allyl (-CH₂-CH=CH₂), phenol (-OH), and methoxy (-OCH₃). Those functional groups allow eugenol to be used as a raw material for the synthesis of other more valuable compounds. For instance, Miao et al. [3] have utilized eugenol as a bio-based heat-resistant epoxy resin. Deng et al. [4] have utilized eugenol as polymeric oil-absorbent microspheres. Meanwhile, Liu et al. [5] have applied eugenol as a bio-renewable thermosetting copolymer.

On the other hand, the helical polyacetylenes have been attracting interests due to their unique structure, chiroptical properties and potentials for being utilized in various critical applications, including as a stimuli-responsive chiral material, enantioselective catalysts, a chemical sensor, chiral discrimination, and optical crystalline material [6]. In poly(*N*-propargylamides) and poly(*N*-propargyl carbamates), the amide groups could stabilize the helical structure by an intramolecular hydrogen

bond as well as steric repulsion between their side chain(s) [7]. In other words, a combination of the steric repulsion and the strengthened intramolecular hydrogen bond will result in a far more stable helical structure.

A recent study demonstrated that poly(*N*-propargyl carbamates) containing eugenol scaffold has been successfully synthesized by using (nbd)Rh⁺[η⁶-C₆H₅B⁻(C₆H₅)₃] catalyst. In fact, the monomer is known to have a splitting methoxy group, where the corresponding polymer would have a moderate molecular weight. If recrystallization is conducted on the monomer until its methoxy group is not splitting anymore, molecular weight (*M_n*) and polydispersity index (PDI) of the monomer will significantly increase. The polymer can function as a smart material [8]. On the other hand, there is another possibility to increase the molecular weight and PDI of a novel derived eugenol having the methoxy group splitting. Shiotsuki et al. [9] revealed that the chiroptical properties of the amino acid based polyacetylenes strongly depend on their molecular weight. Therefore, this study was aimed to prepare novel polymers by introducing eugenol moiety to poly(*N*-propargyl carbamates) and phenylacetylene, which contain carbamate group. In general, this article reports the synthesis and characterization of novel polymers

from derived from eugenol, as a starting material, by utilizing $(\text{nb})\text{Rh}^+[\eta^6\text{-C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3]$ as an effective catalyst in the polymerization of monosubstituted acetylene.

■ EXPERIMENTAL SECTION

Materials

Methyleugenol (4-allyl-2-methoxyphenyl) was provided by Indesso Co., Ltd. 1-(3,4-Dimethoxyphenyl)propane-2-ol was prepared by reacting methyl eugenol with formic acid, which would then be hydrolyzed with potassium hydroxide [10]. Besides, $(\text{nb})\text{Rh}^+[\eta^6\text{-C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3]$ was prepared by reacting $[(\text{nb})\text{RhCl}]_2$ with $\text{NaB}(\text{C}_6\text{H}_5)_4$ [11]. While $[(\text{nb})\text{RhCl}]_2$ was provided by Aldrich, other reagents were commercially provided by Wako Pure Chemical Industries. In this study, tetrahydrofuran (THF) used for polymerization was purified by applying a standard purification procedure.

Instrumentation

The ^1H and ^{13}C NMR spectra were recorded in chloroform-*d* (CDCl_3) on a JEOL EX-400 spectrometer. The IR spectra, on the other hand, were measured by applying a Shimadzu FTIR-8100 spectrophotometer. Furthermore, the melting points were determined with a Yanaco micro melting point apparatus. Carlo Erba 1106 was applied in this study as an elemental analyzer, while Jasco J-810 spectropolarimeter was used to record Circular Dichroism (CD) spectra. The specific rotation $[\alpha]_D$ values were measured on a Jasco DIP-1000 digital polarimeter with a sodium lamp as the light source. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) were estimated by using gel permeation chromatography (GPC) with Shodex K804, K805, and K806 columns eluted with THF as an eluent, polystyrene calibration, refractive-index, and UV detectors.

Procedure

Synthesis of monomers

1-(3,4-Dimethoxyphenyl)propane-2-yl prop-2-ynyl carbamate (1). First, 1-(3,4-dimethoxyphenyl)propane-2-ol (19.6 g, 0.1 mol, 1 equiv.) was added to a solution of tryphosgene (25 g, 0.1 mol 1 equiv.) in dry ether (200 mL) at 0 °C, and the resulting mixture was stirred at the same temperature for 1 h. Next, propargylamide (7.97 g, 0.1 mol,

1 equiv.) was added to the mixture, and the mixture was continuously stirred at 0 °C overnight. After that, a white precipitate was filtered off, and the filtrate was concentrated. Ethyl acetate (100 mL) was later added to the residue. The organic phase was washed with 2 M HCl, saturated with aqueous NaHCO_3 , dried over MgSO_4 , and then concentrated. In the end, monomer **1** was isolated and purified by applying column chromatography with silica gel as solid adsorbent, which was then eluted by using 3/2 (v/v) *n*-hexane/ethyl acetate to form a white solid. Yield: 25%; mp 90–93 °C; $[\alpha]_{D20} = 0^\circ$ ($c = 0.1$ g/dL in CDCl_3). ^1H NMR (400 MHz, CDCl_3 , δ): 1.21–1.37 (m, 3H, CH_3), 2.22 (s, 1H; $\equiv\text{CH}$), 2.53–2.89 (d, $J = 3.4$ Hz, 2H, $-\text{CH}_2\text{-Ar}$), 3.86 (d, $J = 3.4$ Hz, OCH_3), 4.17 (s, 1H, $-\text{NHCO}-$), 4.98–5.02 (m, 2H, $-\text{CH}-$), 6.23 (s, 1H, $-\text{CH}_2\text{-NH}-$), 6.71–6.80 (m, 3H, Ar); ^{13}C NMR (400 MHz, CDCl_3 , δ): 17.1, 19.0, 32.8, 42.3, 53.1, 56.3, 68.3, 71.6, 80.4, 114.9, 115.2, 121.6, 144.9, 147.7, 132.1, 157.5, 175.7; IR (KBr, cm^{-1}): 3320 (N-H), 3291 (H-C \equiv), 1660 (C=O); Anal. calcd. for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_5$: C, 64.97%; H, 6.91%; N, 5.05%; found: C 64.90%, H 6.93%, N 7.73%.

1-(3,4-Dimethoxyphenyl)propane-2-yl 3-ethynyl phenylcarbamate (2). This compound **2** was synthesized from 3-ethynylaniline in a similar manner to **1**. It was later isolated and purified by using column chromatography with silica gel as solid adsorbent, and then eluted by using 3/2 (v/v) hexane/ethyl acetate to form a colorless liquid.

Yield: 30%; bp 185 °C; $[\alpha]_{D20} = 0^\circ$ ($c = 0.1$ g/dL in CDCl_3); ^1H NMR (400 MHz, CDCl_3 , δ): 1.35–1.37 (d, 3H, CH_3), 2.66–2.92 (d, $J = 3.4$ Hz, 2H; $-\text{CH}_2\text{-Ar}$), 3.83 (d, $J = 12.7$ Hz, 6H; OCH_3), 4.05 (s, 1H, CH), 4.52 (s, 1H, CH), 6.74–7.81 (m, 7H, Ar), 9.86 (s, 1H, NH); ^{13}C NMR (400 MHz, CDCl_3 , δ): 21.1, 42.9, 56.1, 71.6, 81.4, 82.3, 112.5, 121.3, 121.4, 112.5, 121.4, 122.9, 126.4, 127.9, 128.5, 130.0, 135.5, 147.1, 152.3, 149.9; IR (CHCl_3 , cm^{-1}): 3322 (N-H), 3290 (H-C \equiv), 1661 (C=O); Anal. calcd. for $\text{C}_{20}\text{H}_{21}\text{NO}_4$: C, 70.78%, H 6.24%, N 4.13%; found: C 70.75%, H 6.25%, N 4.12%.

1-(3,4-Dimethoxyphenyl)propane-2-yl 4-ethynyl phenylcarbamate (3). This compound **3** was synthesized from 4-ethynylaniline in a similar manner to **1**. It was later isolated and purified by applying

column chromatography with silica gel as solid adsorbent, and then eluted by using 3/2 (v/v) hexane/ethyl acetate to form a brown solid.

Yield: 20%; mp/bp 20 °C; $[\alpha]_{D20} = 0^\circ$ ($c = 0.1$ g/dL in $CDCl_3$); 1H NMR (400 MHz, $CDCl_3$, δ): 1.35–1.37 (d, 3H, CH_3), 2.66–2.92 (d, $J = 3.4$ Hz, 2H; $-CH_2-Ar$), 3.83 (d, $J = 4.9$ Hz, 6H; OCH_3), 4.05 (s, 1H, CH), 4.52 (s, 1H, CH), 6.74–7.81 (m, 7H, Ar), 9.86 (s, 1H, NH); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 21.1, 42.9, 56.1, 71.6, 81.4, 82.3, 112.5, 121.3, 121.4, 112.5, 121.4, 122.9, 126.4, 127.9, 128.5, 130.0, 135.5, 147.1, 152.3, 149.9; IR (KBr, cm^{-1}): 3323 (N-H), 3290 (H-C \equiv), 1660 (C=O); Anal. calcd. for $C_{20}H_{21}NO_4$: C, 70.78%, H 6.24%, N 4.13%; found: C 70.79%, H 6.26%, N 4.15%.

(2S)-1-(3,4-Dimethoxyphenyl)propane-2-yl 2-((prop-2-ynyl)carbonylamino)propanoate (4). This compound **4** was synthesized from (S)-2-amino-N-(prop-2-ynyl)propanamide in a similar manner to **1**, in which 1-(3-dimethylaminopropyl)-3-ethyl carbodiimide hydrochloride (EDC.HCl) was applied as a condensing agent. It was later isolated and purified by column chromatography with silica gel as solid adsorbent, and then eluted by using 3/2 (v/v) hexane/ethyl acetate to form a colorless liquid.

Yield: 25%; mp/bp 180 °C; $[\alpha]_{D20} = -7.5^\circ$ ($c = 0.1$ g/dL in $CDCl_3$); 1H NMR (400 MHz, $CDCl_3$, δ): 1.22–1.38 (m, 6H, CH_3), 2.66–2.92 (d, $J = 3.4$ Hz, 2H; $-CH_2-Ar$), 3.83 (d, $J = 4.9$ Hz, 6H; OCH_3), 4.05 (s, 1H, CH), 4.52 (s, 1H, CH), 6.74–7.81 (m, 7H, Ar), 9.86 (s, 1H, NH); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 21.1, 42.9, 56.1, 71.6, 81.4, 82.3, 112.5, 121.3, 121.4, 112.5, 121.4, 122.9, 126.4, 127.9, 128.5, 130.0, 135.5, 147.1, 152.3, 149.9; IR ($CHCl_3$, cm^{-1}): 3323 (N-H), 3290 (H-C \equiv), 1660 (C=O); Anal. calcd. for $C_{18}H_{23}NO_6$: C, 61.88%, H 6.64%, N 4.01%; found: C, 61.89%, H 6.66%, N 4.02%.

Polymerization of monomers 1-4

In this process, a monomer solution ($[monomer] = 0.1$ M) in THF was added to $(nbd)Rh^+[\eta^6-C_6H_5B^-(C_6H_5)_3]$ solution ($[monomer]/[Rh] = 50$) under nitrogen, and it was kept at 30 °C for 1 h. The resulting solution was later poured into *n*-hexane (600 mL) to precipitate a polymer. Next, it was isolated by filtration, which was then dried under a reduced pressure to form a powder.

Polymerization with the addition of menthol

Menthol (1% weight) was added to the monomer solution ($[monomer] = 0.1$ M) in THF. Next, the mixture was added into $(nbd)Rh^+[\eta^6-C_6H_5B^-(C_6H_5)_3]$ solution ($[monomer]/[Rh] = 50$) under nitrogen atmosphere, and then kept at 30 °C for 1 h. The produced solution was later poured into *n*-hexane (600 mL) to precipitate a polymer. Then, it was isolated by using the filtration process, which was followed by a drying process under reduced pressure to form a powder.

Spectroscopic data of the polymers

Poly(1). 1H NMR (400 MHz, $CDCl_3$, δ): 1.09–1.33 (m, 3H, CH_3), 2.53–2.92 (m, 2H, $-CH_2-Ar$), 4.24 (s, 1H, $-NHCO-$), 4.89 (s, 1H, $-CH-CH_3$), 6.59–6.65 (m, 5H, $-CH=C$, NH, Ar); IR ($CHCl_3$): 3430 (N-H), 2980, 2950, 2650 (C=O), 1561.

Poly(2). 1H NMR (400 MHz, $CDCl_3$, δ): 1.35–1.37 (d, 3H, CH_3), 2.66–2.92 (d, $J = 3.4$ Hz, 2H; $-CH_2-Ar$), 3.83 (d, 6H; OCH_3), 4.05 (s, 1H, CH), 5.52 (s, 1H, NH), 6.74–7.81 (m, 7H, Ar); IR ($CHCl_3$): 3432 (N-H), 1733 (C=O), 1512.

Poly(3). 1H NMR (400 MHz, $CDCl_3$, δ): 1.35–1.37 (d, 3H, CH_3), 2.66–2.92 (d, $J = 3.4$ Hz, 2H; $-CH_2-Ar$), 3.83 (d, 6H; OCH_3), 4.05 (s, 1H, CH), 5.55 (s, 1H, NH), 6.74–7.81 (m, 7H, Ar); IR ($CHCl_3$): 3431 (N-H), 17.33 (C=O), 1514.

Poly(4). 1H NMR (400 MHz, $CDCl_3$, δ): 1.09–1.36 (m, 6H, CH_3), 2.64–2.86 (m, 2H, $-CH_2-CH-$), 3.79 (s, 8H, OCH_3 , $CH=CCH_2$), 4.24 (s, 1H, $-CH-NH-$), 4.68 (s, 1H, $-CH-CH_2-Ar$), 5.02 (s, 1H, $-NH$), 6.38 (s, 1H, $-CH=$), 6.65–6.70 (m, 3H, Ar); IR ($CHCl_3$): 3430 (N-H), 1732 (C=O), 1510.

RESULTS AND DISCUSSION

Synthesis of Monomers

The synthetic routes for novel monomers **1-4** was displayed in Fig. 1. First, eugenol derivative was transformed into monomers **1-4** in moderate yield. In addition to elemental analysis, the monomers were identified by 1H NMR and ^{13}C NMR in IR spectroscopy. Apparently, the IR spectra of all monomers showed absorbances from carbamates at 3300–3500 cm^{-1} (N-H) and 1661–1750 cm^{-1} (C=O). The characteristic absorption

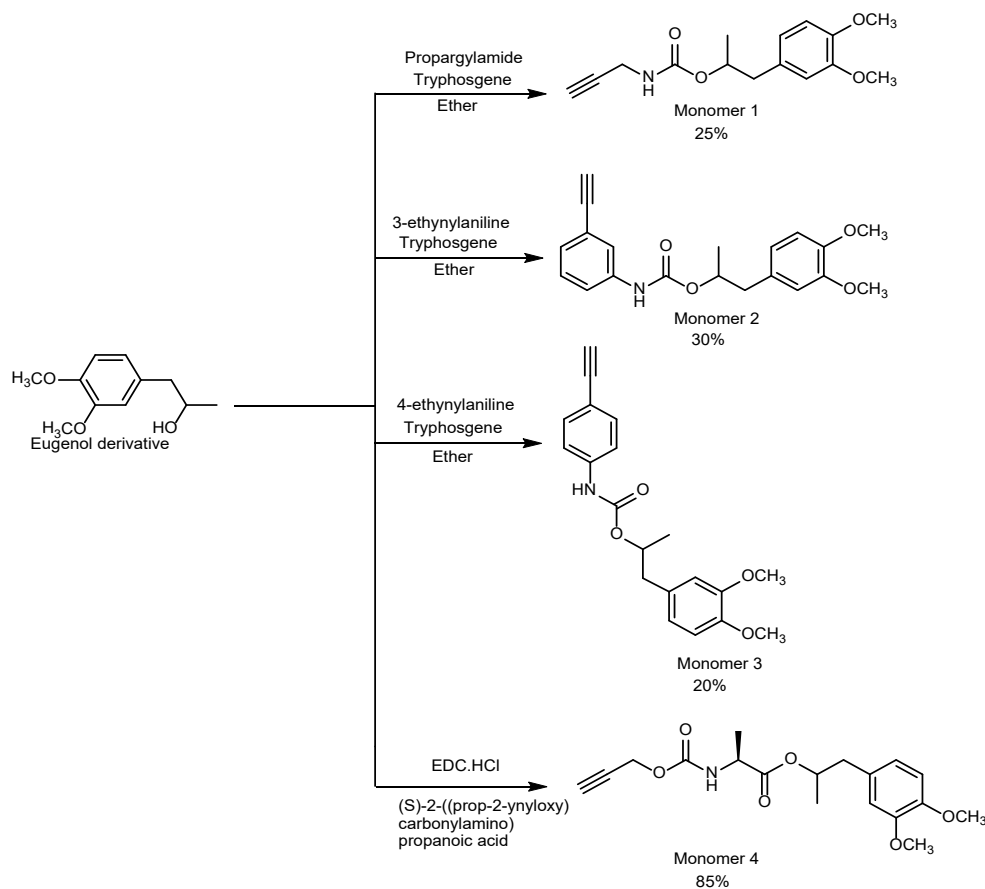


Fig 1. Synthesis of monomers 1-4

of H-C \equiv stretched appeared at 3290 cm⁻¹, while the absorption at 2169 cm⁻¹ showed C \equiv C stretching groups. Furthermore, confirmation of monomer 1-4 structures was conducted by applying ¹H NMR analysis. In fact, the hydrogen resonance at 2.20 ppm showed protons from triple-bond acetylene from monomers. In addition, resonance at about 1.50 and 4.80 ppm showed hydrogen atoms from CH₃ and CH from eugenol derivatives. The resonance at 3.3 ppm was experiencing splitting, which was typical for the methoxy group of eugenol derivative (Fig. 3). In addition, the ¹³C NMR shows the present peak for H-C \equiv , and elemental analyses indicated the monomers had been successfully synthesized.

Polymerization

The polymerization of monomers 1-4 by applying (nbd)Rh⁺[η 6-C₆H₅B⁻(C₆H₅)₃] catalyst, which was particularly effective for the polymerization of monosubstituted acetylenes [12-19], gave the

corresponding poly (1)-(4) in very good yields (Fig. 2). Based on FTIR analysis, the disappearance of absorption for H-C \equiv and C \equiv C at 3390 and 2169 cm⁻¹, showed that triple-bonds from monomers to be completely polymerized. Moreover, the proton resonance of acetylene at 2.22 ppm was, in fact, not visible, showing that polymerization had taken place (Fig. 3). Other polymers poly(1-3)s showed a similar spectra. Practically, polymerizations of 1-4 with the application of Rh catalyst gave the corresponding polymers with molecular weights ranging from 13,900–18,400 g/mol (Table 1).

It is interesting to note that the molecular weight of poly(1) (13,900 g/mol) could be increased by the addition of menthol (Fig. 4). As a matter of fact, this study was the first to report the addition of menthol into (nbd)Rh⁺[η 6-C₆H₅B⁻(C₆H₅)₃] catalyst to significantly increase molecular weight in high quantitative yield (\approx 99%). Monomer 1 was observed to be in a splitting methoxy group, hence the molecular weight of the resulting polymer could be

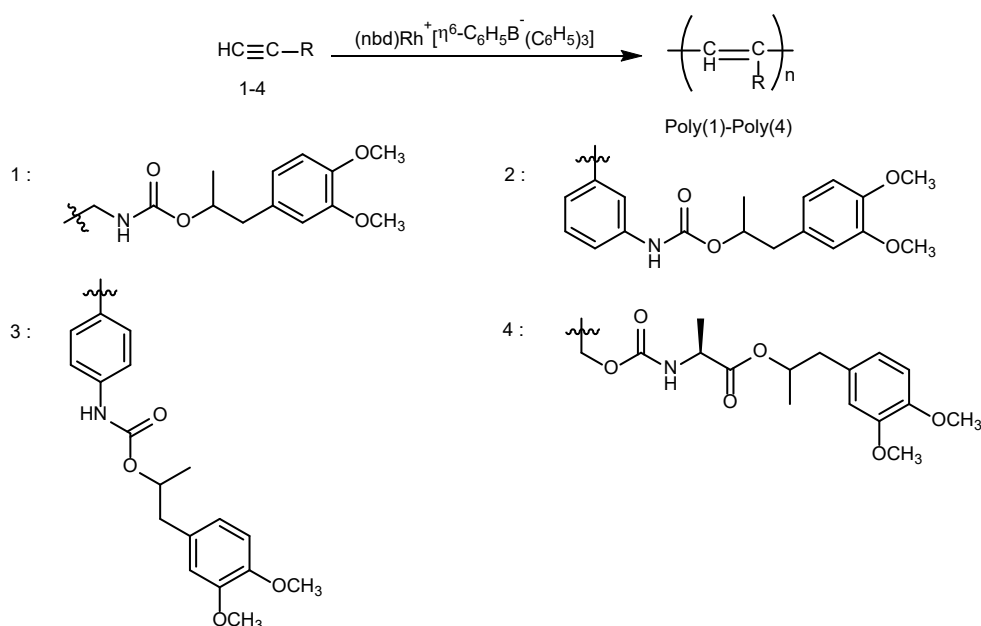


Fig 2. Synthesis of poly(1)-poly(4) using Rh catalyst

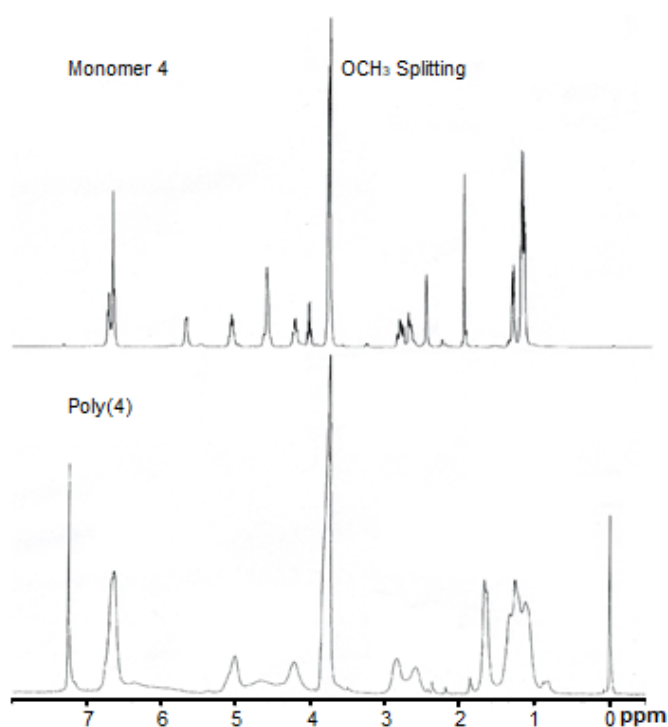


Fig 3. ¹H-NMR spectra of monomer 4 and poly(4)

technically increased. In the work of Rahim [8], the recrystallizing monomer to produce no splitting methoxy group had been proven to increase its molecular weight and PDI significantly. Practically, the addition of menthol may induce the recrystallization of monomer 1; hence, its

Table 1. Polymerization of 1-4 with the application of $[(\text{nbd})\text{Rh}^+[\eta^6\text{-C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3]^a$

Monomer	Polymer			
	Yield	M_n^c	M_w/M_n^c	$[\alpha]_D^{25}$ ^d
1	99	13,900	1.6	0
2	98	18,400	2.4	0
3	97	18,200	2.5	0
4	98	16,400	1.7	350

^a) polymerization conditions $\rightarrow [M]_0 = 0.1 \text{ M}$ in THF; $(\text{nbd})\text{Rh}^+[\eta^6\text{-C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3] = 2 \text{ mM}$; $[M]_0/[\text{Rh}] = 50$; $T = 30 \text{ }^\circ\text{C}$; $t = 1 \text{ h}$

^b) *n*-hexane-insoluble part

^c) determined by GPC (THF elution and polystyrene standards)

^d) measured by polarimetry (concentration = 1 g/dL, CHCl_3)

molecular weight and PDI would significantly increase. From the technical point of view, it would be easier to synthesize the polymer, while the time required to conduct the synthesis would be faster compared to the typical method without recrystallization. In the current situation, rationales behind this finding have not been clear; hence, it requires further works.

Poly(*N*-propargylamides) and poly(*N*-propargyl carbamates) were found to be less stable, which unfortunately limited their applications [7]. In fact, applying an appropriate substituent would increase the stability of their helix. This study found that eugenol may be potentially used as the appropriate substituent. In

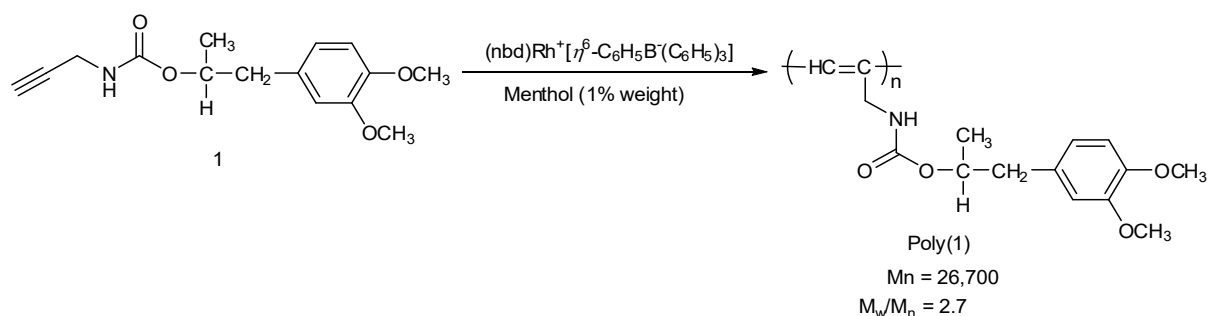


Fig 4. Synthesis of poly(1) in the presence of menthol

Table 2. Solubility of poly(1)-poly(4) in various solvent^a

Solvent	CH ₂ Cl ₂	CHCl ₃	THF	Acetone	Benzene	Toluene	DMF	DMSO	Hexane
Poly(1)	O	O	O	O	O	O	O	O	x
Poly(2)	O	O	O	O	O	O	O	O	x
Poly(3)	O	O	O	O	O	O	O	O	x
Poly(4)	O	O	O	O	O	O	O	O	x

^a O = soluble; x = insoluble (3.0 mg of polymer/1 mL of solvent)

general, the helix content could be tuned by adjusting temperature [9]. In this work, poly(4) showed a large specific rotation, which was indicated by a one-handed helical structure. Meanwhile, poly(1), poly(2), and poly(3) showed no specific rotation, which indicated their helical structures to have a racemic form. In fact, poly(1)-poly(3) were observed to contain eugenol moieties in a racemic form, resulting in 0 (zero) specific rotation. Meanwhile, poly(4) was revealed to contain an optically-active substituent (L-Alanine), and its main chain of polymer helix was stabilized by hydrogen bonding, hence resulting in a very large specific rotation ($[\alpha]_D = -350^\circ$).

Solubility of Polymers

Table 2 shows that poly(1)-poly(4) have very good solubility in various organic solvents. In other words, these polymers could completely dissolve in common solvents, including CH₂Cl₂, CHCl₃, THF, Acetone, Benzene, Toluene, DMF, and DMSO. However, they would not be soluble in *n*-hexane.

The solubility of monosubstituted polyacetylene was, in fact, dependent on their substituent. The poor solubility of monosubstituted polyacetylene could be attributed to the rigid structure and stronger hydrogen bonding strength. As an example, poly(*N*-propargylamides) containing azobenzene and fluorene moieties was not soluble in acetone, benzene, toluene, DMF, or hexane

[7,10]. Thus, polyacetylenes had various drawbacks in their applications. They were particularly insoluble in solvents, making it essentially impossible to process these materials [20]. To address the problem, this study demonstrated that the introduction of the eugenol derivative scaffold might improve the polymer solubility; hence, it would be easily processed.

CONCLUSION

Polymerization of a monomer containing carbamate and eugenol scaffolds in the presence of $[(\text{nbD})\text{Rh}^+[\eta^6\text{-C}_6\text{H}_5\text{B}(\text{C}_6\text{H}_5)_3]$ catalyst gave the corresponding polymers in high yields with the molecular weight ranging from 13,900–18,400 g/mol. Besides, adding menthol to the catalyst has successfully increased molecular weight of the polymers. The polymers were found to be soluble in common organic solvents and have a stable helical structure.

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