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SYNTHESIS OF POLYACETYLENES CONTAINING CINNAMATE AND DERIVED CINNAMATE

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ABSTRACT

This research aimed to investigate the production of polyacetylenes with cinnamate and its derivatives. The polymerization of (*S*)-*N*-(1-oxo-1-(prop-2-ynylamino)propan-2-yl) cinnamamide (**1**) and (*S,E*)-*N*-(1-oxo-1-(prop-2-ynylamino)propan-2-yl)-3-(3,4,5-trimethoxyphenyl)acrylamide (**2**), using the catalyst (nbd)$Rh^+[\eta6\text{-}C_6H_5B^-(C_6H_5)_3]$, generated polyacetylenes [poly(**1**)–poly(**2**)], with a molecular weight range of 5,800- 8,160 g/mol in good yield. The result showed these polymers to be insoluble, except in common organic solvent, and showed large specific rotation. Poly (**1**) and Poly (**2**) were exhibit stable helical structures, with potential application as a chiral catalyst in asymmetric synthesis.

Keywords: Polyacetylenes, Cinnamate, Derived Cinnamate, Chiral Catalyst

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INTRODUCTION

Natural compounds and derivatives of cinnamic (3-phenylpropenoic) acid are assumed to function physiologically by regulating and supporting the development of plants during lignification and suber processes. In addition, there is an extensive combination of acid with hydroxyl by-products, including coumaric, caffeic, and ferulic, and are also believed to be accessible from seeds, leaves, roots, stems, and bark. This structure exists richly in essential oils of several species, e.g. cinnamomic, featuring an aromatic ring and a double bond, in the material's best interest. It is widely applicable as a flavoring agent, perfumery, and pharmaceutical.[1] However, cinnamic acid and hydroxyl derivatives tend to undergo trans-cis isomerization or dimerization based on a [2 + 2] cycloaddition reaction, followed by the formation of a cyclobutene ring, after UV irradiation treatment.[2-3] Furthermore, the functional groups allowed the acid to promote the synthesis of other valuable compounds.[4-5] Recent reports show the successful synthesis of polymers containing cinnamic acid[6], to be subsequently applied as a base material in the linear polyester and copolyester synthesis[7], with photoluminescence properties. On the other hand, optically active helical polyacetylenes and derivatives are interesting for application catalysts towards asymmetric reactions, chiral selectors for inducing enantioselective crystallization, and chiral carriers for enantio differentiating release. They are promising for practical applications in chiral-related science and technologies. The poly (N-Propargylamide) component can initiate stabilization in the helical structure, through a combination of intramolecular hydrogen bonds and steric rejection.[8] This is achieved because of the crosslinking activity between the acid side chains.

In a recent study, the synthesized poly(*N*-propargylamides) comprises of the pendulous thiourea groups, in the presence of a catalyst (nbd)$Rh^+[\eta6\text{-}C_6H_5B^-(C_6H_5)_3]$, while helical polymers estimated to be optically active service as a chiral organocatalyst for Michael reaction.[9] These novel polymers are incorporated with naturally derived cinnamic acid and poly (*N*-propargylamides) with useful, green, sustainable applications. Previous reports have shown the product synthesis and evaluated the intrinsic properties, by examining the effectiveness of monosubstituted acetylene polymerization, with the catalyst (nbd)$Rh^+[\eta6\text{-}C_6H_5B^-(C_6H_5)_3]$.

EXPERIMENTAL

Materials

Natural and derived cinnamic acid, Chloroform-d ($CDCl_3$), THF-d8, 4-methylmorpholine, N- (BOC) -L-Alanine, HCl, THF, propargylamine, $NaHCO_3$, anhydrous $MgSO_4$, $CHCl_2$, TFA, isobutyl chloroformate,

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silica gel, hexane, ethyl acetate were purchased from Wako Pure Chemical Industries, including $[(nbd)RhCl]_2$ and $NaB(C_6H_5)_4$. The preparation of $(nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ involved a reaction between $NaB(C_6H_5)_4$ and $[(nbd)RhCl]_2$[10,11], while THF was purified for application during polymerization, through a standard procedure.

Instrumentation

Chloroform-d ($CDCl_3$) and THF-d8 were evaluated to attain the ^1H and ^{13}C NMR spectra using JEOL EX-400 spectrometer, while the spectrophotometer (Shimadzu FTIR-8100) measured IR spectra. The melting points determination involved a Yanaco micro apparatus, while Carlo Erba 1106 was used for elemental analysis. In addition, Jasco J810 spectropolarimeter was utilized to detail the values for specific rotation $[\alpha]_D$ were documented on a digital polarimeter (Jasco DIP-1000), and sodium lamp was adopted as a light source. Furthermore, the weight-average (M_w) and number-average (M_n) molecular weights, were assessed through gel permeation chromatography (GPC), comprising Shodex K804, K805, and K806 column, while tetrahydrofuran (THF) served as the eluent, flow rate 0.35 mL/min. In addition, the unit encompasses polystyrene calibration, UV detectors, and refractive index.

Monomer Synthesis

(*S*)-*N*-(1-oxo-1-(prop-2-ynylamino) propan-2-yl) cinnamamide (1)

4-methylmorpholine (3.41 mL, 33, mmol) and N- (BOC) -L-Alanine (7.97 g, 25.5 mmol) were added to THF (100 mL) at 0 ºC. Propargylamine (2.33 mL, 33.8 mmol) was introduced after 15 minutes to obtain a white solid concentrate. The residue generated was treated with 2 M HCl, 100 mL of ethyl acetate, alongside saturated $NaHCO_3$ water solution, before further drying with anhydrous $MgSO_4$. Furthermore, 50 grams of Propargylamide-L-Alanine-BOC combined with $CHCl_2$ solvent was transferred to the TFA to produce amine compounds by involving isobutyl chloroformate. Therefore, propargylamide was acquired by monomer 1 and isolated before the purification process. This involved column chromatography with silica gel, adopted in the liberation of 3/2 (v/v) hexane/ethyl acetate yielding a white solid form.

Yield: 95%: mp 75-77 °C; $[\alpha]_{D20}$ = - 4.1º (c = 0.1 g/dL in $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$, ppm): 1.48 (d, 3H, CH_3), 3.08 (s, 1H; $\equiv CH$), 3.94 (d, 2H,-CH_2-), 3.94 (m,1H,-CH-), 6.31 (s,1H,-NHCO-), 6.46 (d,1H,-CH=), 6.71-6.80 (m,3H,Ar), 7.60 (d,1H,-CH=); ^{13}C NMR (400 MHz, $CDCl_3$, ppm): 17.9, 29.9, 48.3, 73.2, 80.1, 124.0, 127.9, 128.5, 135.2, 147.7, 166.8, 172.0; IR (KBr, cm^{-1}): 3320 (N-H), 3291 ($H-C\equiv$), 1724 (C=O);. Anal. calcd. for $C_{15}H_{16}N_2O_2$: C, 70.29%; H, 6.29%; N, 10.93%; found: C 70.27%, H 6.30%, N 10.95%.

(*S,E*)-*N*-(1-oxo-1-(prop-2-ynylamino) propan-2-yl)-3-(3,4,5-trimethoxyphenyl) acrylamide (2)

The title compound was synthesized from methoxy cinnamic acid, as against cinnamic acid, using a process similar to monomer 1.

Yield : 92%: mp 88-90 °C; $[\alpha]_{D20}$ = - 5.0 º (c = 0.1g/dL in $CDCl_3$); ^1H NMR (400 MHz, $CDCl_3$, ppm): 1.48 (d, 3H, CH_3), 3.08 (s, 1H; $\equiv CH$), 3.83 (s, 9H; OCH_3), 3.94 (s,2H,-CH_2-) ,4.71 (m,1H, CH), 6.31 (s,1H,-NHCO-), 6.46 (d,1H,-CH=), 6.78 (s,2H,Ar), 7.40 (d,1H,-CH=); ^{13}C NMR (400 MHz, $CDCl_3$, ppm): 17.9, 29.9, 48.3, 56.1, 60.8, 73.2, 80.1, 103.8, 124.0, 130.3, 138.4, 141.7, 153.0, 166.8, 172.0; IR ($CHCl_3$, cm^{-1}): 3322 (N-H), 3290 ($H-C\equiv$), 1725 (C=O);. Anal. calcd. for $C_{18}H_{22}N_2O_5$: C,62.42%, H 6.40%, N 8.09%; found: C 62,44%, H 6.41%, N 8.10%.

Polymerization

A solution of ([monomer] = 0.1 M) in THF was mixed with $(nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ ([monomer]/[Rh] = 50) in the presence of nitrogen and reserved at 30ºC for 1h. The liquid generated was incorporated with hexane (600 mL) to achieve precipitated polymers. This product was subsequently filtered before drying under lowered pressure.

Spectroscopic Data of the Polymers

Poly(1)

^1H NMR (400 MHz, THF-d8, ppm): 1.43 (s, 3H, CH_3), 3.72 (s, 1H, -CH-), 4.61 (s, 2H, -CH_2-), 4.74 (s, 1H, -CH-), 6.18 (s, 1H, -CH=C-), 6.69-6.68 (d, 1H, -CH=CH-), 7.35-7.69 (m, 3H, Ar), 7.84-7.89 (d, 1H, -CH=CH-), 8.41 (s, -NH-CO), 8.65 (s, -NH-CO-) ; IR (THF, cm^{-1}): 3430 (N-H), 1730 (C=O), 1561.

Poly(2)
^{1}H NMR (400 MHz, THF-d8, ppm): 1.43 (s, 3H, CH_3), 2.59 (s, 9H; OCH_3), 3.75 (s, 1H, -CH-), 3.39 (s,2H,-CH_2-) ,4.52 (s,1H, -CH=C-), 6.33-6.37 (d, 1H, -CH=CH-), 6.87-6.97 (d, 2H, Ar), 7.29 (s, 1H, -NH-CO), 7.53-7.57 (d, 1H, -CH=CH-), 8.49 (s, 1H, -NH-) ; IR (THF, cm^{-1}): 3432 (N-H), 1733 (C=O), 1561

RESULTS AND DISCUSSION

Monomer Synthesis

Figure-1 illustrates the synthesis routes for novel monomers 1-2 generated from the natural and derived cinnamic acid. The yield was moderate, based on the identification with ^{13}C NMR, ^{1}H NMR, IR spectroscopy, and elemental analysis. In addition, IR spectra showed absorbance at 3300 – 3500, and 1661 - 1750 cm^{-1} with the absorption of N-H and C = O, respectively from amide. Meanwhile, the absorption characteristics of H−C≡ stretched at 3290 cm^{-1} and 2169 cm^{-1} presented C≡C extended groups. The monomer 1-2 structures were confirmed through the ^{1}H NMR analysis, where 3.08 ppm hydrogen resonance showed the presence of protons at the triple bond of acetylene. Furthermore, the resonance of 6.50 ppm and 7.80 ppm indicates hydrogen atoms at CH generated from cinnamic acid and the derivatives, while ^{13}C NMR evaluation demonstrated a current peak of H-C≡, and elemental analysis showed successful synthesis.

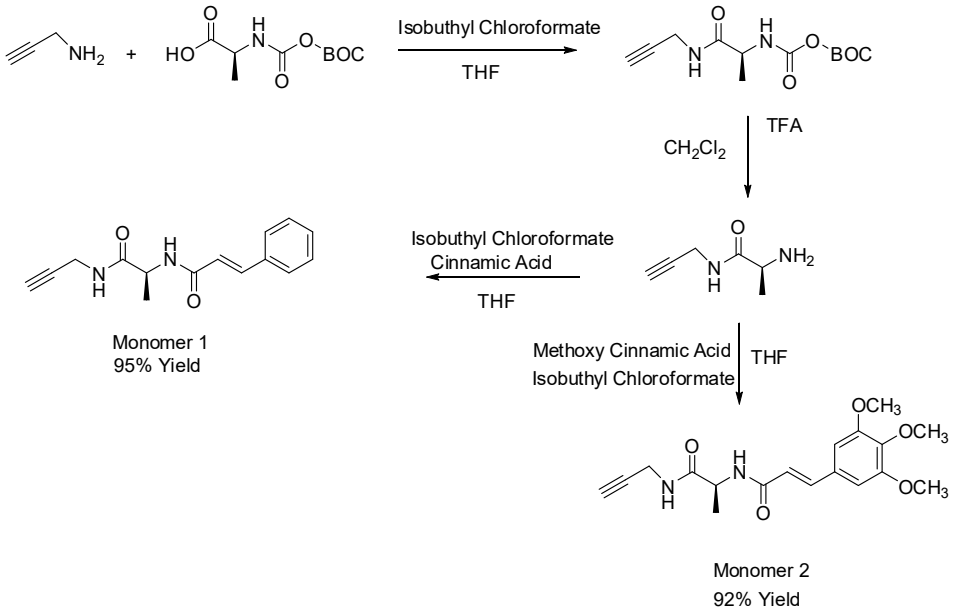

Fig.-1: Schematic Monomer Synthesis of **1** and **2**

Polymerization

Table-1 showed the effective polymerization of monomer **1-2** with Rh catalyst. Rh catalyst is an effective catalyst for polymerization monosubstituted acetylenes[12-17]. This process also applied to monosubstituted acetylenes and the loss of absorption H−C≡ and C≡C stretched at 3390 and 2169 cm^{-1} shows the complete polymerization of triple bonds. In addition, the invisible resonance at 2.22 ppm designating the acetylene proton was evidence of a positive reaction. Figure-2 highlighted the proton resonance of cinnamate at 3.78 ppm and 4.42 ppm, evident due to dimerization, with further visibility at 6.65 ppm; 6.69 ppm, 7.83 ppm, and 7.89 ppm, while other polymers, poly (**2**), displayed a similar spectrum. The monomers 1-2 were subjected to polymerization, using the catalyst (nbd)$Rh^+[\eta 6\text{-}C_6H_5B^-(C_6H_5)_3]$, and thus delivered a good yield of products with molecular weight ranging between 5,800 - 8,160 g/mol. Figurer-3 was showed polymerization of monomers **1** and **2** with (nbd)$Rh^+[\eta 6\text{-}C_6H_5B^-(C_6H_5)_3]$ catalyst. This polymerization was corresponding to cinnamate moieties in the side chain and crosslinking of cinnamate.

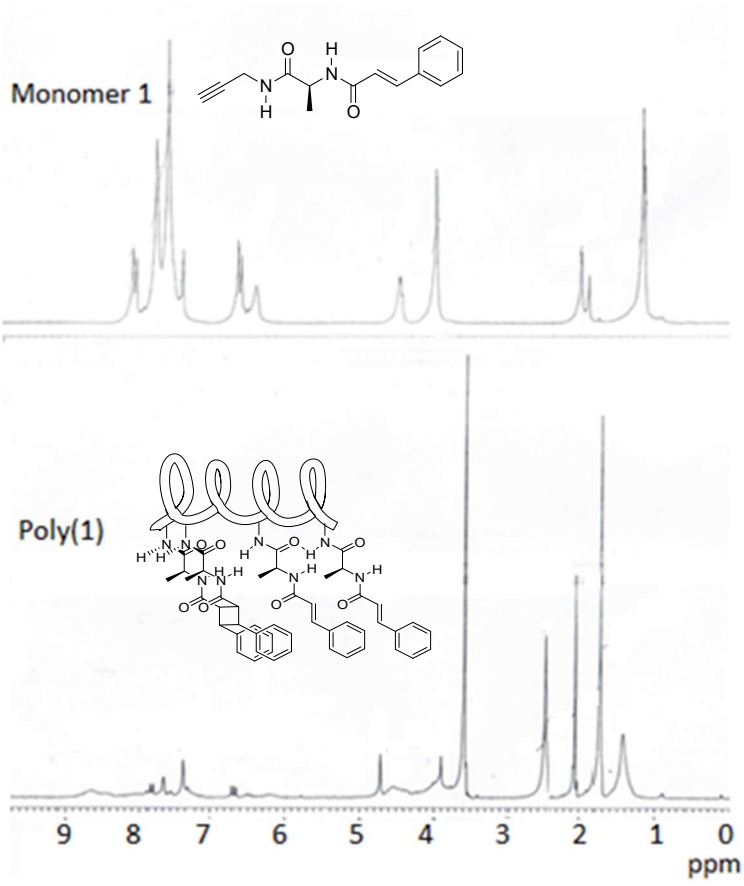

Fig.-2: ^{1}H NMR of Monomer **1** and Poly (**1**)

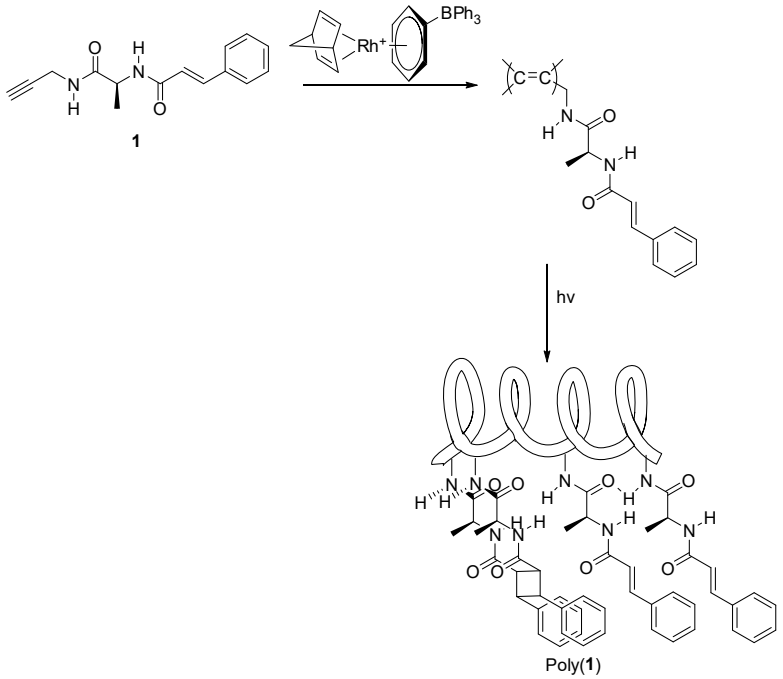

Fig.-3: Schematic Synthesis of Poly (**1**)

Poly(*N*-Propargylamides) demonstrated low stability due to limited application, although the helix with appropriate substituent showed an increase. Furthermore, poly (**1**)-poly (**2**) showed large specific rotation indicated by a one-handed helical structure, containing an optically active substituent (L-Alanine).

Meanwhile, the main polymer chain relatively formed a helix and provided stability, resulting from hydrogen bonding, thus showing a large specific rotation ($[\alpha]_D$ = - 500°).

Table-1: Polymerization of 1-2 With [(nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$][a]

Monomer	Polymer[b]				
	Yield	M_n[c]	M_w[c]	M_w/M_n[c]	$[\alpha]_D$ (°)[d]
1	99	2,320	5,800	2.5	- 500
2	98	3,400	8,160	2.4	- 530

[a] Polymerization conditions: $[M]_0$ = 0.1 M in THF; (nbd)Rh$^+$[η^6-$C_6H_5B^-(C_6H_5)_3$] = 2 mM; $[M]_0/[Rh]$ = 50; temperature = 30 °C; and time = 1 h. [b] Hexane-insoluble part. [c] Determined by GPC (THF discharge and polystyrene standards). [d] Measured by polarimetry (concentration = 1 g/dL, THF).

Solubility of Polymers

Table-2 showed poly (**1**)-poly (**2**) to be not soluble, despite the complete polymer dissolution in commonly used solvents, including benzene, THF, and toluene. However, total insolubility was observed with CH_2Cl_2, $CHCl_3$, DMF, acetone, hexane, and DMSO. The monosubstituted polyacetylene was poorly soluble because of the strong hydrogen bonds and structural rigidity, for example, poly(*N*-Propargylamides) containing azobenzene and insoluble fluorene moieties in acetone, benzene, toluene, DMF, and hexane. In addition, organic synthesis also involved several soluble and stimuli-responsive catalytic systems.[18,20]

Table-2: Solubility of Poly(**1**)-Poly(**2**)[a]

Solvent	CH_2Cl_2	$CHCl_3$	THF	Acetone	Benzene	Toluene	DMF	DMSO	Hexane
Poly(1)	x	x	o	x	o	O	x	x	x
Poly(2)	x	x	o	x	o	O	x	x	x

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

CONCLUSION

Based on the results and discussion, polymerization of polyacetylenes containing cinnamic acid and the derivatives produced a high yield of corresponding polymers, in a range of 2,300-3,400 g/mol, following the incidence of dimerization. However, the main polymer chain relatively formed a helix and provided stability, thus showing a large specific rotation ($[\alpha]_D$=- 500°) and characterized by solubility in commonly used organic solvents.

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