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Unique Polymerization and New Smart Material of Eugenol-Based Helical Polymers

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Abstract: ***The series of eugenol–based helical polymers were synthesized. The polymerization of 1–4 with Rh catalyst gave the corresponding polyacetylene [poly(1)–poly(4)] in different yield and a molecular weight ranging from 5,000-11,000. Splitting of methoxy (OCH$_3$) group which is indicated of conformational isomerization cis-trans like amide group of eugenol part affected to polymerization yield and M_n. Polymerization monomer 1 and 2 is not easy, but polymerization of 3 and 4 gives high yield and M_n of the polymer. These polymers were soluble in common organic solvent and shown stable helical structure. Eugenol-based optically active helical polyacetylene catalysts as a new smart material have been synthesized. The new smart material was observed when measured in ^{1}H NMR; proton NH moves when cursor move to the peak of NH. This is because of spontan crystallization and isomerization of methoxy group of crystal chiral of eugenol part. These properties make this catalyst as a new smart material.***

Keywords: Conformational isomerization, Methoxy group, Eugenol-Based Polymers, Rh

1. Introduction

Intelligent polymers are polymers that can only respond to small external stimuli. These small external stimuli include UV irradiation, pH, temperature, magnetic fields etc.[1] Self-healing smart polymers are a new class of smart materials that have the ability to repair themselves when they are damaged without the need to use detection or repair using manual interventions of any type. The increasing demand for fuel oil stocks used to produce polymers and the need for polymer materials with improved performance in challenging applications continues to drive the need for materials with longer durability. On the other hand, Indonesia is one of the largest essential oil producers in the world. Nearly half of the world's consumption of clove leaf oil comes from Indonesia. The content of eugenol, or more correctly is called 3- (4-hydroxy-3-methoxyphenyl) propene, from oil, is about 80-90% by weight.[2-3]

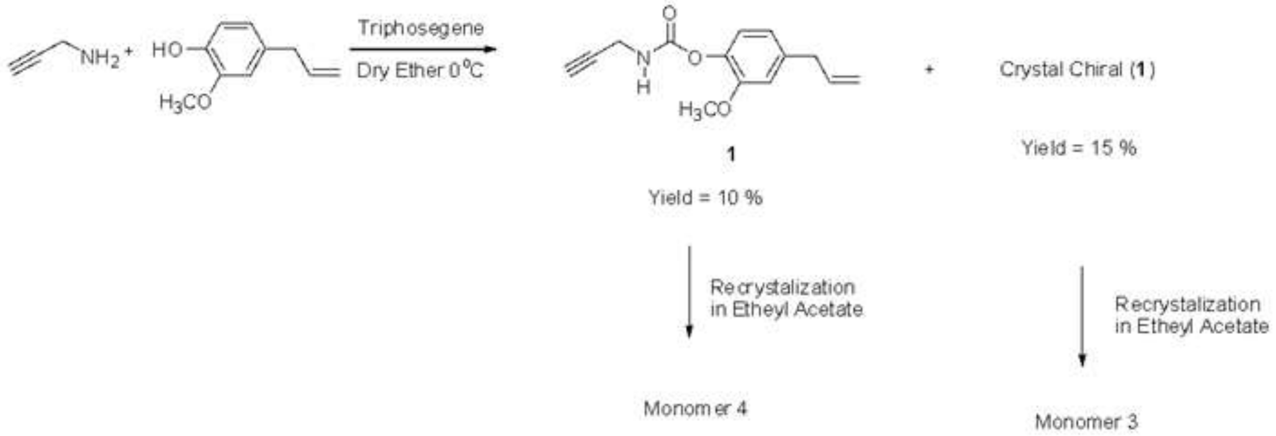
One of interesting in synthesis optically active compound is absolute asymmetric synthesis. This synthesis can be produced crystal chiral. This crystal can be spontaneous crystallization.[4-6] This property interesting from the spontaneous properties. Stability of Poly (*N*-Propargylamides) dan Poly(*N*-Propargilcarbamate) less stable so the application is limited.[7] With appropriate substituent the stability of helix increased and we found that eugenol is the appropriate substituent. Organometallic polymerization catalysts have been extensively studied since the most important method using transition metal catalysts for polymer synthesis was discovered by Ziegler and Natta in the 1950s.[1]

One of interesting in organometallic polymerization is living polymerization, which is molecular weight can be controlled and low polydispersity index. Rh-catalyzed living polymerization of PA was first accomplished by Noyori and coworkers in 1994.[2] Later, Masuda et al. revealed that [(nbd)RhCl]2–Ph2C=(Ph)Li–PPh3 provided the polymer whose *M*w/ *Mn* was about 1.1 and that its initiation efficiency with respect to Rh was virtually quantitative.[3] Rh catalysts are capable of producing stereoregular substituted polyacetylenes with all-*cis* or *cis*-rich main chain, which enables the formation of the predominantly one-handed helical structure by incorporation of chiral groups into polymer side chains. Polymerization helical poly(*N*-Propagylamides) and poly(*N*-Propargylcarbamates) are mainly doing using with (nbd)Rh$^+$[η^6-C$_6$H$_5$B$^-$(C$_6$H$_5$)$_3$].[4] Polimerisasi Poliasetlene with Eugenol moiety with Rhodium catalyst is interesting because different with general trend, i.e. the polymerization with phenylacetylenes with [(nbd)RhCl]$_2$ in the present Et$_3$N is effective to increase yield and M_n but for polyacetylene containing eugenol moiety reduced the M_n and the yield different.[5-6]

This paper reports the synthesis and report a new smart material properties of helical polymers from eugenol as starting material and examination of polymerization with (nbd)Rh$^+$[η^6-C$_6$H$_5$B$^-$(C$_6$H$_5$)$_3$] catalyst, which is effective to polymerization monosubstituted acetylene.

2. Results and Discussion

Monomer Synthesis



Scheme 1: Synthesis of Monomer 1-4

Scheme 1 illustrated the synthesis routes for novel monomer 1-4. Eugenol was transformed into monomer 1-4 in moderate yield. The reaction is corresponding crystal chiral in quantitative yield. Before recrystallization, the monomer 1 and 2 have small differences in ^{1}H NMR. (Figure 1 and 2) but after recrystallization, the ^{1}H NMR of monomer 3 and 4 were the same (Figure 3 and 4). The monomers were identified by ^{1}H NMR and ^{13}C NMR and IR spectroscopy, in addition to elemental analysis.

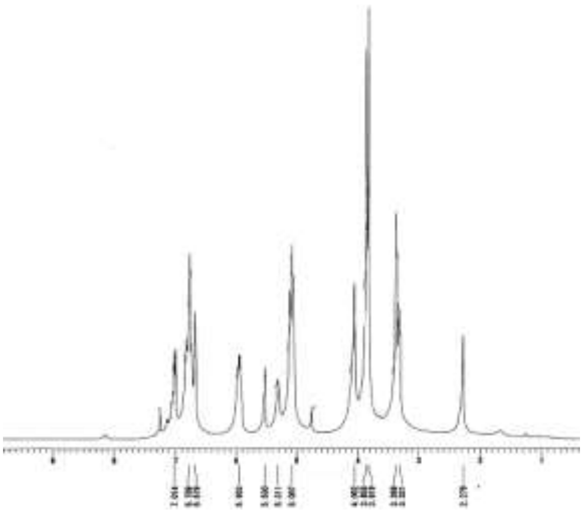


Figure 1: ^{1}H NMR of Crystal Chiral of **1** (Monomer **1**)

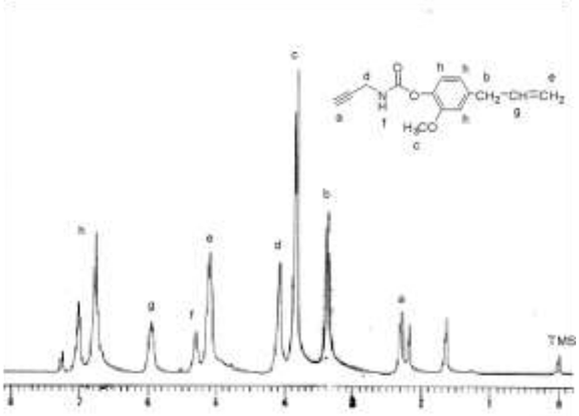


Figure 2: ^{1}H NMR of Eugenol-Based Acetylenes of **1** (Monomer **2**)

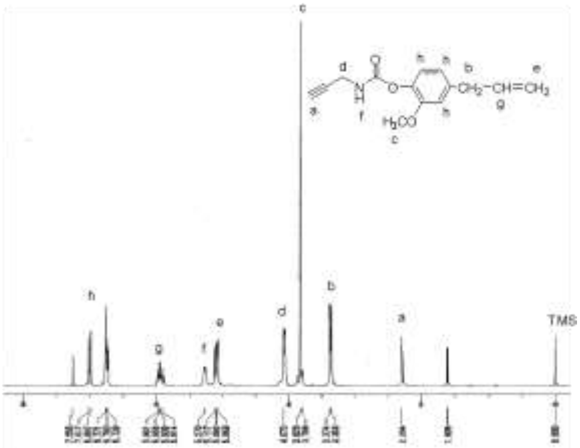


Figure 3: ^{1}H NMR of Eugenol-Based Acetylenes of **1** after recrystallization (Monomer **3**)

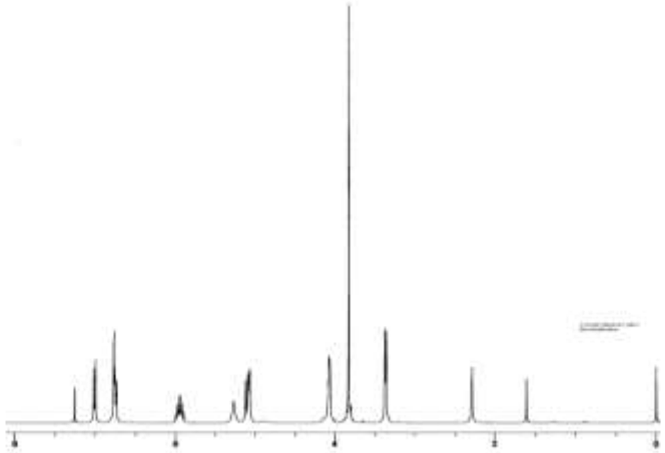
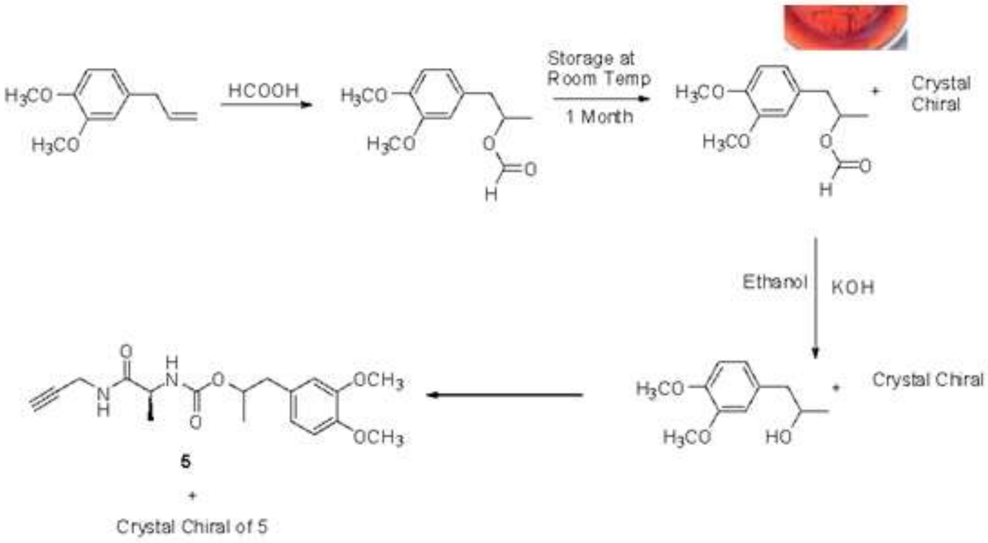


Figure 4: 1H NMR of Crystal Chiral of Eugenol-Based Acetylenes of 1 (Monomer **4**)



Scheme 2: Synthesis of Monomer 5 and crystal chiral of 5

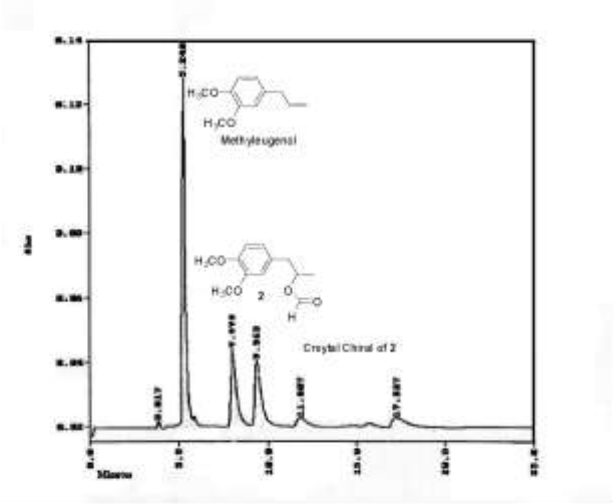


Figure 5: HPLC analysis of eugenol derivated after one month with HPCL

Analysis of ester of methyleugenol and formic acid with HPLC column chiral after one month showed that crystal chiral was formed (Figure 5). The monomers were identified by ^{1}H NMR and ^{13}C NMR and IR spectroscopy, in addition to elemental analysis.

Polymerization

^{1}H NMR in Figure 1 and Figure 2 were shown the conformational transition of eugenol based monomer. Methoxy group was splitting which is indicated the conformational transition of eugenol. Figure 3 was shown that after crystallization methoxy group cannot split. Polymerization of monomer 1-4 was different in yield and M_n. Different splitting of methoxy group corresponding polymer with different yield, *M*n. Polymerization of not conformational isomerization of eugenol part can be yielded the polymer with high molecular weight. (Table 1). Interesting part when the structure of crystal chiral (Figure 3) and not crystal chiral (Figure 4) were polymerization in the same condition yielded the polymer in different yield, molecular weight, and polydispersity. The formation of crystal chiral and formation of new Rh+ catalyst in crystal chiral is the reason why polymerization of polyacetylene with Rh catalyst different with the general trend.

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

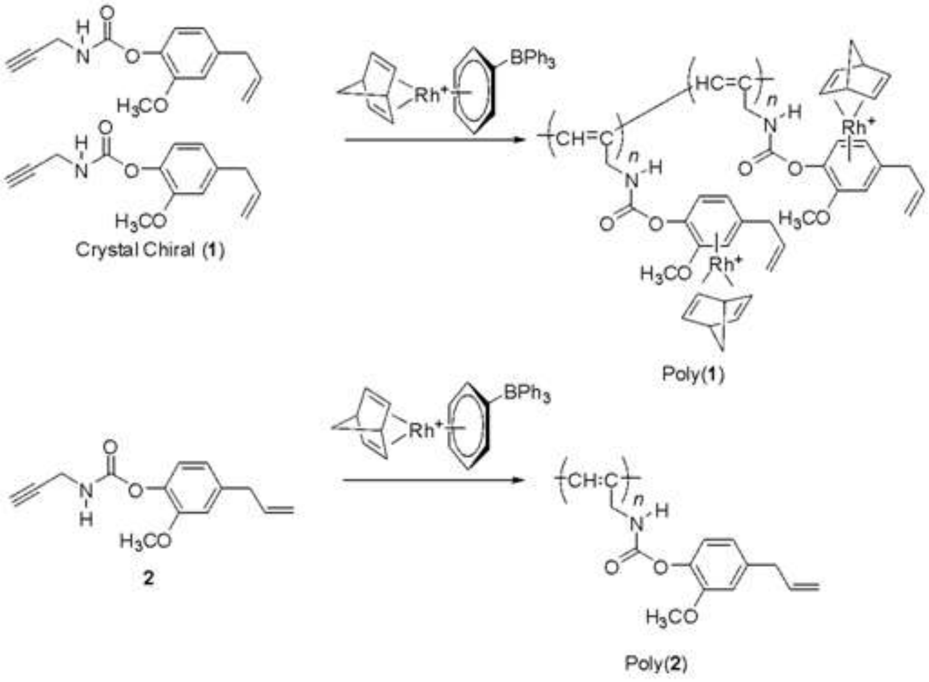
Monomer	polymer				
	J(OCH$_3$) (Hz)	Color	Mn	Mw/Mn	[α]D (o)
1	14.9	White	5,000	2.2	0
2	11.6	Orange	6,000	2.0	0
3	0	Brown	11,000	2.5	0
4	0	Light brown	9200	1.9	0

[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 oC; and time = 1 h. . [b] Hexane-insoluble part. [c] Determined by GPC (THF elution and polystyrene standards). [d] Measured by polarimetry (concentration = 1 g/dL, $CHCl_3$).

Figure 5 was shown the 1H NMR of Poly(1) and found that the polymer containing rhodium with norbornadiene (Scheme 2). Crystal chiral of monomer 3 is also containing a catalyst.

The rhodium bound to catalyst was observed with need eyes when the catalyst was casting from a solution. From a literature, we also found that polymer containing eugenol part very effective to bond transition metal catalyst. Figure 2 was shown the CD spectrum of catalyst from this CD spectrum this catalyst was formed a helical structure with a stable structure. The helical structure can be tuned by temperature. These properties this catalyst belong to the smart material. Scheme 1 as shown in the synthesis of the catalyst.

Stability of Poly (*N*-Propargylamides) dan Poly(*N*-Propargilcarbamate) less stable so the application is limited.[8] With appropriate substituent, the stability of helix increased and we found that eugenol is the appropriate substituent. The helices content can be tuned by temperature and stable until 90 °C. These entire polymers are soluble in common organic solvent including CH_2Cl_2, $CHCl_3$, THF, Acetone, Benena, Toluene, DMF, and DMSO.



Scheme 3: Polymerization of Crystal Chiral of 1 and monomer 2

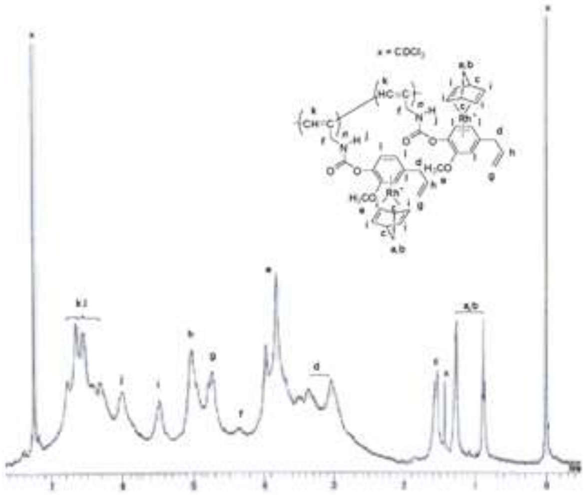
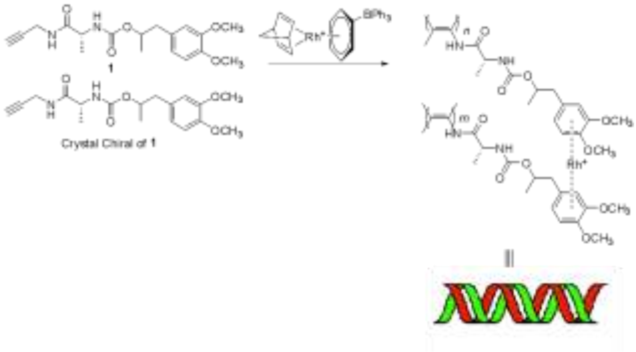


Figure 6: 1H NMR of Poly(1)



Scheme 4: Polymerization of Crystal Chiral of 5 and Monomer 5

New Smart Material

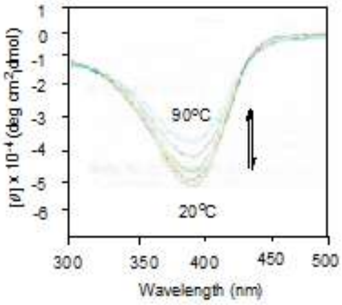


Figure 6: CD Spectrum of Catalyst measured in Toluene at 20°C-90°C

The rhodium bound to catalyst was observed with naked eyes when the catalyst was casting from a solution. From a literature, we also found that polymer containing eugenol part very effective to bond transition metal catalyst.[9]

The helical catalyst in ^{1}H NMR was shown that proton NH moves before cursor at the position of proton amid group. These polymers can be categorized as a new smart material. It may be applied as smart material at large magnetic fields. This is because of spontaneous crystallization and isomerization of crystal chiral of eugenol part. Optically active eugenol-based helical polymers catalysts are material in the future. This catalyst was partly soluble in water due to the presence of crystal chiral of **1**. Polymerization of eugenol-based acetylenes with $[(nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]]$ were corresponding catalyst with M_n=17,000 (PDI=2.0). This catalyst have very large specific rotation $[\alpha]_D$ = -2000°

Experimental Measurements

^{1}H and ^{13}C NMR spectra were recorded in chloroform-d ($CDCl_3$) on a JEOL EX-400 spectrometer. IR spectra were measured on a Shimadzu FTIR-8100 spectrophotometer. The melting points were measured on a Yanaco micro melting point apparatus. Elemental analyses were carried out at the Gadjah Mada University. The specific rotation ($[\alpha]_D$) values were measured on a Jasco DIP-1000 digital polarimeter with sodium lamp as a light source. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) were estimated by gel permeation chromatography (GPC) with Shodex K804, K805, and K806 column eluted with tetrahydrofuran (THF) as an eluent, polystyrene calibration, and refractive-index and UV detectors. HPLC analysis was using Pircle`s chiral column eluted with hexane: isopropanol as eluent, at 30°C, and UV detector.

Materials

Eugenol (4-allyl-2-methoxyphenol) was obtained from Indesso Co., Ltd. $(nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ was prepared by reaction of $[(nbd)RhCl]_2$ with $NaB(C_6H_5)_4$ as described in the literature.[7] $[(nbd)RhCl]_2$ was purchased from Aldrich. Other reagents were purchased from Wako

Pure Chemical Industries. All the reagents in the monomer synthesis were used as purchased without purification. THF used for polymerization were purified by the standard procedure.

Monomer Synthesis

4-allyl-2-methoxyphenyl prop-2-ynylcarbamate (1)-(4)

Eugenol (19.6 g, 1 mmol) was added to a solution of triphosgene (25 g, 0.084 mol) in dry ether at 0 ^oC, and the resulting mixture was stirrer that temperature for 1 h. Propargylamide (7.97 g, 25.5 mmol) was added to the mixture, and it was continued stirring 0 ^oC overnight. A white precipitate was filtered off, and the filtrate was concentrated. Ethyl acetate (100 mL) was added to the residue, and the organic phase was washed with 2 M HCl and saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated. Monomer **1-2** was isolated and purified by silica ge column chromatography eluted with 3/2 (v/v) hexane/ethyl acetate as white solid. Monomer **3-4** was obtained by recrystallization of monomer **1** and **2** in ethylacetate.

Monomer **1** Yield: 15%: mp 90-93 °C; $[\alpha]_D^{20} = 0^0$ (c = 0.1 g/dL in $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$, δ): 1.21-1.37 (m, 6H, CH_3), 2.22 (s, 1H; ≡CH), 2.53-2.89 (d, J = 3.4 Hz, 2H,-CH_2-Ar), 3.86 (d, J = 3.4 Hz, OCH_3), 4.03 (s,2H, -CH_2-NH-), 4.17 (s,1H,-NHCO-), 4.98-5.02 (m,2H,-CH-), 6.23 (s,1H,-CH2-NH-), 6.23 [s,1H,-CH(CH)$_3$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≡), 1660 (C=O);. Anal. calcd. for $C_{18}H_{24}N_2O_5$: C 62.05, H 6.94, N 8.04; found: C 62.13, H 6.93, N 7.73.

Monomer **2** Yield: 10%: mp 90-93 °C; $[\alpha]_D^{20} = 0^0$ (c = 0.1 g/dL in $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$, δ): 1.21-1.37 (m, 6H, CH_3), 2.22 (s, 1H; ≡CH), 2.53-2.89 (d, J = 3.4 Hz, 2H,-CH_2-Ar), 3.86 (d, J = 3.4 Hz, OCH_3), 4.03 (s,2H, -CH_2-NH-), 4.17 (s,1H,-NHCO-), 4.98-5.02 (m,2H,-CH-), 6.23 (s,1H,-CH2-NH-), 6.23 [s,1H,-CH(CH)$_3$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≡), 1660 (C=O);. Anal. calcd. for $C_{18}H_{24}N_2O_5$: C 62.05, H 6.94, N 8.04; found: C 62.13, H 6.93, N 7.73.

Monomer **3** Yield: 14%: mp 90-93 °C; $[\alpha]_D^{20} = 0^0$ (c = 0.1 g/dL in $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$, δ): 1.21-1.37 (m, 6H, CH_3), 2.22 (s, 1H; ≡CH), 2.53-2.89 (d, J = 3.4 Hz, 2H,-CH_2-Ar), 3.86 (d, J = 3.4 Hz, OCH_3), 4.03 (s,2H, -CH_2-NH-), 4.17 (s,1H,-NHCO-), 4.98-5.02 (m,2H,-CH-), 6.23 (s,1H,-CH2-NH-), 6.23 [s,1H,-CH(CH)$_3$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≡), 1660 (C=O);. Anal. calcd. for $C_{18}H_{24}N_2O_5$: C 62.05, H 6.94, N 8.04; found: C 62.13, H 6.93, N 7.73.

Monomer **4** Yield: 10%: mp 90-93 °C; $[\alpha]_D^{20} = 0^0$ (c = 0.1 g/dL in $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$, δ): 1.21-1.37 (m, 6H, CH_3), 2.22 (s, 1H; ≡CH), 2.53-2.89 (d, J = 3.4 Hz, 2H,-CH_2-Ar), 3.86 (d, J = 3.4 Hz, OCH_3), 4.03 (s,2H, -CH_2-NH-), 4.17 (s,1H,-NHCO-), 4.98-5.02 (m,2H,-CH-), 6.23 (s,1H,-CH2-NH-), 6.23 [s,1H,-CH(CH)$_3$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≡), 1660 (C=O);. Anal. calcd. for $C_{18}H_{24}N_2O_5$: C 62.05, H 6.94, N 8.04; found: C 62.13, H 6.93, N 7.73.

1-(3,4-dimethoxyphenyl)propan-2-yl(S)-oxo-1-(prop-2-ynylamino)propan-2-ylcarbamate (5)

1-(3,4-dimethoxyphenyl)-propan-2-ol (19.6 g, 1 mmol) was added to a solution of triphosgene (25 g, 0.084 mol) in dry ether at 0 ^oC, and the resulting mixture was stirrer that temperature for 1 h. (S)-2-amino-*N*-(prop-2-ynyl) propanamide (7.97 g, 25.5 mmol) was added to the mixture, and it was continued stirring 0 ^oC overnight. A white precipitate was filtered off, and the filtrate was concentrated. Ethyl acetate (100 mL) was added to the residue, and the organic phase was washed with 2 M HCl and saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated. Monomer **5** was isolated and purified by silica gel column chromatography eluted with 3/2 (v/v) hexane/ethyl acetate as white solid.

Yield: 75%: mp 90-93 °C; $[\alpha]_D^{20} = -5.2^0$ (c = 0.1 g/dL in $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$, δ): 1.21-1.37 (m, 6H, CH_3), 2.22 (s, 1H; ≡CH), 2.53-2.89 (d, J = 3.4 Hz, 2H,-CH_2-Ar), 3.86 (d, J = 3.4 Hz, OCH_3), 4.03 (s,2H, -CH_2-NH-), 4.17 (s,1H,-NHCO-), 4.98-5.02 (m,2H,-CH-), 6.23 (s,1H,-CH2-NH-), 6.23 [s,1H,-CH(CH)$_3$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≡), 1660 (C=O);. Anal. calcd. for $C_{18}H_{24}N_2O_5$: C 62.05, H 6.94, N 8.04; found: C 62.13, H 6.93, N 7.73.

Polymerization

A monomer solution in THF was added to a solution $(nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ ([monomer/[Rh] = 50) under nitrogen, and the solution was kept at 30^{o}C for 1h. The resulting solution was poured into hexane (600 mL) to precipitate a polymer. It was isolated by filtration followed by drying under reduced pressure as a powder.

Spectroscopic Data of the Polymers

Poly(1)

^1H NMR (400 MHz, $CDCl_3$, δ): 3.21 (d, 2H, CH_2), 3.83 (d, J =11,6 Hz, 3H; OCH_3), 3.97 (s,1H, CH_2), 4.98-5.00 (s,2H,CH_2), 5,92 (s,1H, CH), 6.00 (s,1H, NH), 6.76-7,08 (m, 3H,Ar), 8.00 (s,1H, NH); IR ($CHCl_3$): 3434 (N-H), 17.33 (C=O), 1515.

Poly(2)

^1H NMR (400 MHz, $CDCl_3$, δ): 3.21 (d, 2H, CH_2), 3.83 (d, J =11,6 Hz, 3H; OCH_3), 3.97 (s,1H, CH_2), 4.98-5.00

(s,2H,CH_2), 5,92 (s,1H, CH), 6.00 (s,1H, NH), 6.76-7,08 (m, 3H,Ar), 8.00 (s,1H, NH); IR ($CHCl_3$): 3434 (N-H), 17.33 (C=O), 1515

Poly(3)
^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.21 (d, 2H, CH_2), 3.83 (d, *J* =11,6 Hz, 3H; OCH_3), 3.97 (s,1H, CH_2), 4.98-5.00 (s,2H,CH_2), 5,92 (s,1H, CH), 6.00 (s,1H, NH), 6.76-7,08 (m, 3H,Ar), 8.00 (s,1H, NH); IR ($CHCl_3$): 3434 (N-H), 17.33 (C=O), 1515.

Poly(4)
^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.21 (d, 2H, CH_2), 3.83 (d, *J* =11,6 Hz, 3H; OCH_3), 3.97 (s,1H, CH_2), 4.98-5.00 (s,2H,CH_2), 5,92 (s,1H, CH), 6.00 (s,1H, NH), 6.76-7,08 (m, 3H,Ar), 8.00 (s,1H, NH); IR ($CHCl_3$): 3434 (N-H), 17.33 (C=O), 1515.

Poly(5)
^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.09-1.33 (m, 6H, CH_3), 2.53-2.92 (m, 2H, -CH_2-Ar), 3.68-3.89 (s, 8H, CH=CCH_2), 4.24 (s, 1H, -NHCOO-), 4.89 (s, 2H, -CH-NH, -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.

3. Conclusions

Polymerization of eugenol-based helical polyacetylene is a new type of polymerization and belongs in the unique polymerization. The presence of crystal chiral make the Rh catalyst bound to the polymer and cannot be separate from the polymer. The polymers were shown the stable helical structure and can be function as smart material. The catalyst as a new type of catalyst which is containing crystal chiral. This catalyst was shown the stable helical structure and can be function as catalyst as well as new smart material.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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