

SYNTHESIS OF NOVEL BI-FUNCTIONAL COPOLYMER BEARING STERICALLY HINDERED PHENOL AND HINDERED AMINE GROUPS VIA RING-OPENING METATHESIS POLYMERIZATION*

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Abstract Norbornene derivatives *exo,endo*-2-[2-(3,5-di-*tert*-butyl-4-hydroxyphenoxy)-acetoxy]methyl-5-norbornene (**M1**) and 3,3,5,5-tetramethyl-4-piperidinyl 5-norbornene-*exo,endo*-2-carboxylate (**M2**) were synthesized and polymerized by $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$ to prepare a novel kind of bi-functional polymer bearing sterically hindered phenol (SHP) and hindered amine (HLAS) groups *via* ring-opening metathesis polymerization (ROMP). The resulting copolymers were characterized by gel permeation chromatography (GPC), $^1\text{H-NMR}$ and differential scanning calorimetry (DSC). The number average molecular weight (M_n) and functional unit content of the resulting copolymer could be regulated by varying the concentration of catalyst and monomer feed.

Keywords: Sterically hindered phenol; Hindered amine; Ring-opening metathesis polymerization (ROMP).

INTRODUCTION

It was well known that sterically hindered phenol (SHP) was an efficient radical scavenging group to prevent polymer from oxidation, and hindered amine (HALS) was an efficient light stabilization group. Additives bearing SHP or HALS were usually added into products together in a certain ratio depending on employment situation to prevent them from degradation caused by oxygen, processing and ultraviolet, which was particular to some special demanding applications such as outdoor film, rigorous employment environments and so on. In addition, it should be mentioned that in order to achieve long-term stabilizing effect and avoid potential toxicity caused by physical loss of additives, polymeric stabilizers have gained much interest to minimize the physical loss and to enhance compatibility and durability in recent years^[1, 2]. Copolymerization of monomers bearing SHP and HALS groups prepare bi-functional polymers, which was an efficient way to combine the above two merits. The resulting polymers could be applied as polymeric stabilizers, self-stabilized polymer and radical scavenging resin. Taking advantage of ring-opening metathesis polymerization, the molecular weight and functional unit content could be regulated to satisfy different requirements corresponding to employment situation.

In our previous research, a series of hindered phenol functionalized norbornene monomers with different structure were synthesized and homopolymerized by Grubbs 1st catalyst^[3, 4]. It was inferred that side chain structure with high electronic donating substituent in para position of phenol should have higher efficiency to scavenge radical. Therefore, a novel norbornene derivative, *exo,endo*-2-[2-(3,5-di-*tert*-butyl-4-hydroxyphenoxy)-acetoxy]methyl-5-norbornene (**M1**), containing oxygen substituent in para position of phenol was synthesized and used as one of comonomers in present research. 3,3,5,5-Tetramethyl-4-piperidinyl 5-

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norbornene-*exo,endo*-2-carboxylate (**M2**) functionalized by HALS was synthesized and copolymerized with **M1** by sequential addition *via* ring opening metathesis polymerization (ROMP) to give a novel bi-functional copolymer. Present work investigated copolymerization behavior and showed an efficient way to regulate molecular weight and function unit content of the resulting copolymers.

EXPERIMENTAL

Materials

Sodium borohydride (NaBH_4), 5-norbornene-2-methanol (98%, mixture of *endo* and *exo*) and Grubbs 1st generation catalyst were available from Aldrich. Dichloromethane (Kokusan Chemical) were dehydrated by standard methods before use. 2,6-Di-*tert*-butyl-phenol, 2,2,6,6-tetramethyl-4-hydroxy piperidine, tetraisopropyl orthotitanate, sodium chloroacetate and the other reagents were purchased from Tokyo Chemical and were used without further purification.

Measurements

¹H-NMR spectra were recorded on a JEOL JNM-AL300 spectrometer. Melting point and the glass-transition temperature (T_g) were determined by a SHIMADZU DSC-60 differential scanning calorimeter (DSC). A heating rate of 10°C/min and nitrogen atmosphere was consistently employed. The number average molecular weights (M_n) and polydispersity index (PDI) of the polymers were determined with a JASCO gel permeation chromatography (GPC) equipped with a Shodex K-805L chromatograph column and a JASCO RI-2031 detector, using chloroform as an eluent at a flow rate of 1.0 mL/min, calibrated by polystyrene standards at 40°C.

Monomer Synthesis

3,5-Di-*tert*-butyl-4-hydroxyphenoxyacetic acid

To the mixture of 2,6-di-*tert*-butyl-1,4-hydroquinone (11.1 g; 0.05 mol)^[5, 6], sodium chloroacetate (6.15 g, 0.053 mol), isopropanol (22 mL) and water (25 mL), 4.2 g of 50% sodium hydroxide was added rapidly with stirring under nitrogen atmosphere at room temperature. The reaction mixture was stirred at 95°C for 7 h and then cooled to room temperature. 75 mL of water and 55 mL of ether are added. The ether layer was washed with water (55 mL) and 10% sodium bicarbonate (10 mL). The ether layer was diluted with 25 mL of ether and washed a second time with 20 mL of 10% sodium bicarbonate. The ether layer was discarded and the combined aqueous layers are acidified with 11 mL of hydrochloric acid (6 mol/L) to pH 2. The precipitated acid was filtered, washed with water and dried to give product. (7.5 g; 53.6% yield). mp: 164°C. ¹H-NMR (CDCl_3 , 400 MHz, δ): 6.78 (s, 2H, Ar—H), 4.88 (s, 1H, Ar—OH), 4.59 (s, 2H, —CH₂—), 1.41 (s, 18H, *t*-Bu).

3,5-Di-*tert*-butyl-4-hydroxyphenoxyacetyl chloride

To the solution of 3, 5-di-*tert*-butyl-4-hydroxyphenoxyacetic acid (4.2 g; 0.015 mol) in chloroform (50 mL), thionyl chloride (4.5 mL) was added dropwise with stirring under nitrogen atmosphere at room temperature during a period of 15 min. Then, the reaction mixture was heated to reflux for 6 h and then was allowed to cool. Remove of the chloroform and redundant thionyl chloride under reduced pressure left yellowish crystalline product which was used in next reaction without further purification. ¹H-NMR (CDCl_3 , 400 MHz, δ): 6.76 (s, 2H, Ar—H), 4.91 (s, 1H, Ar—OH), 4.85 (s, 2H, —CH₂—), 1.41 (s, 18H, *t*-Bu).

Exo,endo-2-[2-(3,5-di-*tert*-butyl-4-hydroxyphenoxy)-acetoxy]methyl-5-norbornene (**M1**)

To a solution of *exo, endo*-2-methanol-5-norbornene (1.86 g; 0.015 mol) and pyridine (1.42 g; 0.018 mol) in dichloromethane (15 mL), a solution of the above 3, 5-di-*tert*-butyl-4-hydroxyphenoxyacetyl chloride in 20 mL of dichloromethane was added dropwise with stirring at 0–5°C under nitrogen atmosphere during a period of 20 min, which was accompanied by white precipitation of pyridine salt. The mixture was stirred for 24 h at room temperature and then filtered. After wash once with distilled water (50 mL), saturated sodium bicarbonate solution (50 mL) and twice with distilled water (25 mL) in sequence, the organic phase was separated, dried over anhydrous magnesium sulfate and filtered. Remove of the dichloromethane under reduced pressure left

yellow viscous oil. Recrystallization from 1:10 (*V:V*) ethyl acetate/hexane solvent under refrigeration gave the product. (4.8 g; 82.9% yield). mp: 75°C. ¹H-NMR (CDCl₃, 300 MHz, δ): 6.76 (s, 2H, Ar-H), 5.85–6.14 (m, 2H, —CH=CH—), 4.80 (s, 1H, —OH), 4.56–4.57 (d, 2H, ²*J* 3 Hz, —OCH₂COO—), 3.72–4.26 (m, 2H, —OCOCH₂—), 2.33–2.79 (m, 3H, —CH— in 1,2,4 position of norbornene ring), 0.50–1.84 (m, 22H, *t*-Bu, —CH₂— in 3,7 position of norbornene ring).

3,3,5,5-Tetramethyl-4-piperidinyl acrylate (MAP)

2,2,6,6-Tetramethyl-4-hydroxy piperidine (4.7 g; 0.03 mol), methyl acrylate (6.1 mL) and tetraisopropyl orthotitanate (0.8 mL) were mixed with toluene (100 mL). After being stirred at 90°C for 1 h and then at 120°C for 6 h under nitrogen atmosphere, the reaction solution was cooled to room temperature and quenched by water (10 mL). The organic phase was separated, dried over anhydrous magnesium sulfate and filtered. Remove of the toluene under reduced pressure left yellow viscous oil. Recrystallization from hexane under refrigeration gave product. (5.1 g; 80.6% yield). mp: 52°C. ¹H-NMR (CDCl₃, 300 MHz, δ): 6.29–6.35 (dd, 1H, *J*₂ = 3 Hz, *J*₃ = 15 Hz, *cis*—HC=CCOO—), 5.99–6.08 (q, 1H, *J*₃ = 9 Hz, *J*₃ = 9 Hz, C=CHCOO—), 5.72–5.76 (d d, 1H, *J*₂ = 3 Hz, *J*₃ = 9 Hz, *trans*—HC=CCOO—), 5.17–5.24 (m, 1H, —OCOCH—), 1.49–2.10 (m, 4H, —CH₂—), 1.10–1.19 (d, 12H, *J*₃ = 27 Hz, CH₃).

3,3,5,5-Tetramethyl-4-piperidinyl 5-norbornene-*exo,endo*-2-carboxylate (M2)

To a solution of 3,3,5,5-tetramethyl-4-piperidinyl acrylate (5.0 g; 0.024 mol) in 50 mL of toluene, cyclopentadiene (3.2 g; 0.048 mol) was added dropwise with stirring under nitrogen atmosphere at 0–5°C during a period of 15 min. The reaction mixture was stirred overnight with ice-water bath, and then was stirred at 40°C for 1 h and refluxed for 4 h in sequence. Remove of the toluene under reduced pressure left yellow viscous oil. Recrystallization from hexane under refrigeration gave product. (3.6 g; 54.2% yield). mp: 65°C. ¹H-NMR (CDCl₃, 300 MHz, δ): 5.90–6.19 (m, 2H, —CH=CH—), 5.07–5.18 (m, 1H, —OCOCH—), 2.89–3.17 (m, 3H, —CH— in 1,2,4 position of norbornene ring), 1.10–2.18 (m, 20H, CH₃, —CH₂— of piperidine and —CH₂— in 3,7 position of norbornene ring).

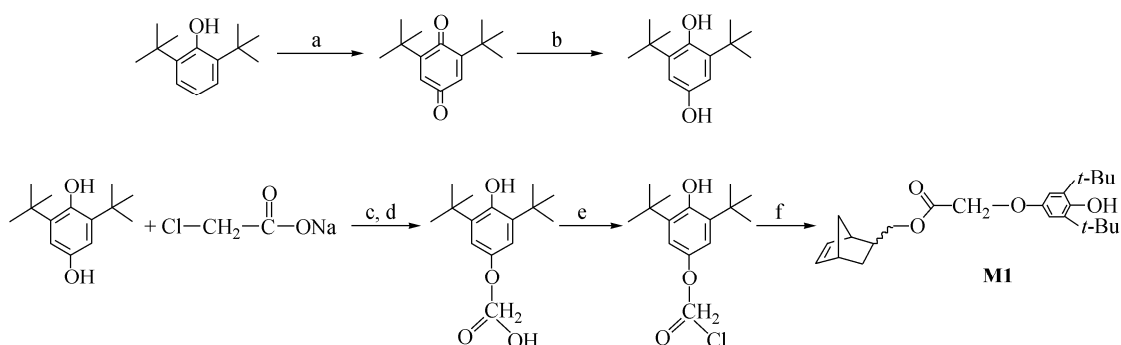
Copolymerization Procedure

In a typical experiment (Scheme 3), a 25 mL flask was charged with **M1** (0.20 g; 0.518 mmol) and 2.46 mL of dichloromethane under nitrogen atmosphere. 0.64 mL of Grubbs 1st catalyst dichloromethane solution (8 mmol/L) was added into the flask by syringe in sequence. After being stirred at room temperature for 3 h, 2 mL of **M2** dichloromethane solution (0.1 g/mL) was added and stirred for another 1 h. Then, ethyl vinyl ether (0.3 mL) was added to the mixture to quench the reaction. The resulting polymer was precipitated in excess of hexane and purified by reprecipitation from chloroform and hexane. The reprecipitated polymer was collected and then dried under vacuum at 30°C for 6 h to yield 0.29 g copolymer as a white solid.

RESULTS AND DISCUSSION

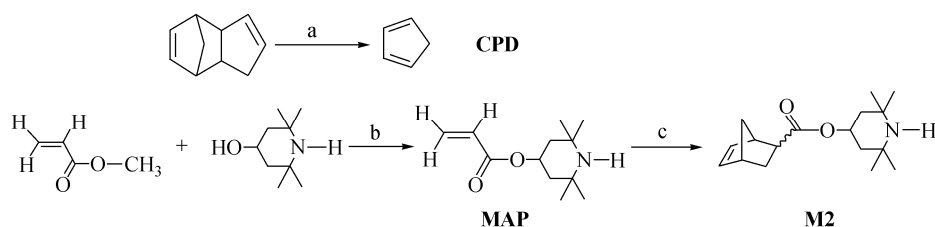
Monomer Synthesis and Characterization

Comonomers **M1** bearing SHP group was synthesized *via* the procedure outlined in Scheme 1. The strategy for **M1** was based on an acylation reaction of 2-methanol-5-norbornene with acid chloride derivative 3,5-di-*tert*-butyl-4-hydroxyphenoxyacetyl chloride, which was prepared from 2,6-di-*tert*-butyl-phenol *via* Jones oxidation (Scheme 1a)^[5], reduction (Scheme 1b)^[6], condensation (Scheme 1c), acidification (Scheme 1d) and chlorination in sequence. Acrylate derivative 3,3,5,5-tetramethyl-4-piperidinyl acrylate was synthesized *via* ester exchange reaction catalyzed by [(CH₃)₂CHO]₄Ti and was used as functionalized dienophile for the Diels-Alder cycloaddition reaction with cyclopentadiene to give comonomer **M2** bearing HALS group (Scheme 2). Unfortunately, the *exo-endo* mixture of the **M2** cycloaddition adduct was not separable by selective recrystallization. The ¹H-NMR signals of olefinic proton appeared in the range of δ = 5.90–6.19 as three batches of peaks indicated the existence of two isomers in **M2**. Likewise for **M1**, there are three batches of proton peaks observed in the range of δ = 5.85–6.14 due to the existence of *endo* and *exo* isomers.



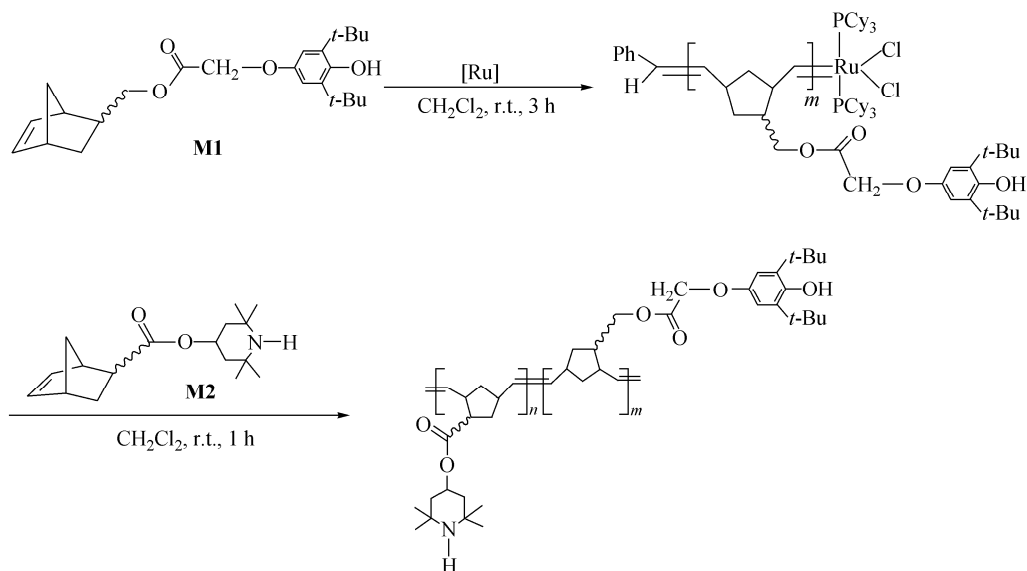
Scheme 1 Synthesis of comonomer **M1**

- a) $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, H_2SO_4 , $\text{Et}_2\text{O}/\text{H}_2\text{O}$, r.t., 24 h; b) NaH_4B , methanol, HCl , r.t., 30 min;
 c) NaOH , *iso*-propanol, H_2O , 95°C , 7 h; d) HCl ; e) SOCl_2 , CHCl_3 , reflux, 6 h;
 f) *exo*, *endo*-2-methanol-5-norbornene, pyridine, CH_2Cl_2



Scheme 2 Synthesis of comonomer **M2**

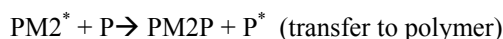
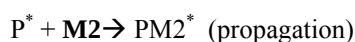
- a) 180°C ; b) $[(\text{CH}_3)_2\text{CHO}]_4\text{Ti}$, toluene, 90°C 1 h, then 120°C 6 h; c) **CPD**, toluene, 0 – 5°C dropwise, 40°C 1 h, then reflux 4 h



Scheme 3 Copolymerization procedure

Copolymerization and Characterization

A typical copolymerization sequence followed for the preparation of bi-functional copolymer was given in Scheme 3. The decision of reaction times in sequential copolymerization was based on ensuring essentially complete polymerization of monomer **M1** in the first step under every molar ratio of **M1** to catalyst ($[M1]/[C]$) varying from 100 to 1000. Following the full conversion of **M1**, different **M2** feed as 0.2 g or 0.05 g was added to continue sequential copolymerization for 1 h. Table 1 summarized the results of the polymerization at various monomer feed ratios using the Grubbs 1st generation catalyst in CH_2Cl_2 at room temperature. Polymers and copolymers prepared from monomer **M1** and **M2** were characterized by ^1H -NMR (Fig. 1) and DSC. The ROMP of **M1** gave polymer **PM1** in high yield (100%) in 3 h in every case of $[M1]/[C]$ studied. The M_n of resulting polymer **PM1** was increased drastically from 4.95×10^4 to 58.33×10^4 when $[M1]/[C]$ increased from 100 to 1000. An *endo* isomer is much less reactive than the corresponding *exo* isomers generally^[7, 8], and therefore two kinds of propagating species with different reactivity formed during polymerization of **M1**, which gave rise to a relative broad PDI (1.20–2.31)^[9]. Additionally, it seems that slow initiation compared with propagation also caused broadening of the PDIs^[10]. Although the copolymerization was carried out by a sequential addition, the M_n did not increase as we expected. Moreover, the difference of M_n between the **PM1** and the following copolymer **PM1M2** initiated by **PM1** became larger and larger with the increase of $[M1]/[C]$ ratio irrespective of **M2** feed. Accompanied by the decline of M_n , PDI also changed a little bit. The copolymerization did not proceed in a block-like way, during which some chain scission reaction occurred presumably. Given the present results, it is concluded that the random copolymer was resulted from chain transfer to polymer during the polymerization. It can also be inferred that the living catalyst centre not only coordinates double bonds of the monomers (leading to propagation), but also coordinates double bonds of the polymer (leading to secondary metathesis such as back-biting, crossing metathesis with another chain). The two possible reactions can be written formally as:



Where P^* represents a living chain, $PM2^*$ represents a polymer chain with a **M2** living terminal. Norbornene monomer bearing 2-*endo*-carbonyl substituent has relatively low ROMP reactivity, which has been proved in literatures^[4, 8, 11]. So, herein, due to the low ROMP reactivity of **M2** and rapid transfer reaction, **M2** unit was introduced into copolymer chain at the sacrifice of chain scission. The result of ^1H -NMR analysis (Fig. 1 and Fig. 2) indicated that when copolymerization carried out in a low catalyst concentration, a relative smaller

Table 1. Copolymerization of **M1** and **M2** by sequential addition

Run	Monomer feed (g)		$[M1]/[C]$	T^a (h)	Yield (g)	Unit content ^b (mol%)		M_n^c ($\times 10^4$)	M_w/M_n^c	T_g (°C)
	M1	M2				M1	M2			
1	0.20	—	100	3	0.20	100.0	—	4.95	1.79	77.2
2	0.20	0.20	100	3 + 1	0.29	59.3	40.7	4.46	1.29	50.7
3	0.20	0.05	100	3 + 1	0.24	79.8	20.2	4.41	1.33	51.5
4	0.20	—	205	3	0.20	100.0	—	9.88	1.20	75.8
5	0.20	0.20	205	3 + 1	0.24	76.1	23.9	7.69	1.42	51.9
6	0.20	0.05	205	3 + 1	0.22	88.8	11.2	8.12	1.45	53.3
7	0.20	—	508	3	0.20	100.0	—	20.89	1.42	75.7
8	0.20	0.20	508	3 + 1	0.21	87.2	12.8	17.46	1.39	54.2
9	0.20	0.05	508	3 + 1	0.21	94.3	5.7	17.81	1.28	56.3
10	0.20	—	1000	3	0.20	100.0	—	58.33	2.31	77.3
11	0.20	0.20	1000	3 + 1	0.20	97.4	2.6	38.88	1.77	77.1
12	0.20	0.05	1000	3 + 1	0.20	97.4	2.6	32.98	1.72	76.8

^a Reaction times in sequence; ^b Determined by ^1H -NMR; ^c Part resolved in chloroform; Determined by GPC calibrated with polystyrene standards

quantity of living species resulted in a lower **M2** unit ratio. Certainly, high **M2** feed was favorable to improving **M2** unit content. However, when copolymerization was subjected to 1000 of $[M1]/[C]$ ratio, just a little **M2** (2.6 mol%) units were introduced into copolymer chain irrespective of **M2** feed. It is the fact that a random copolymer of **M1** and **M2** was obtained, which was different from the expected block copolymer, but it is still interesting to anticipate the potential stabilization effect. Used as polymeric stabilizers, two kinds of function groups of random copolymer should cooperate with each other more closely and effectively. Random dispersion should avoid separation of two kinds of function groups into different parts of base resin, and then bring their stabilization effect into full play.

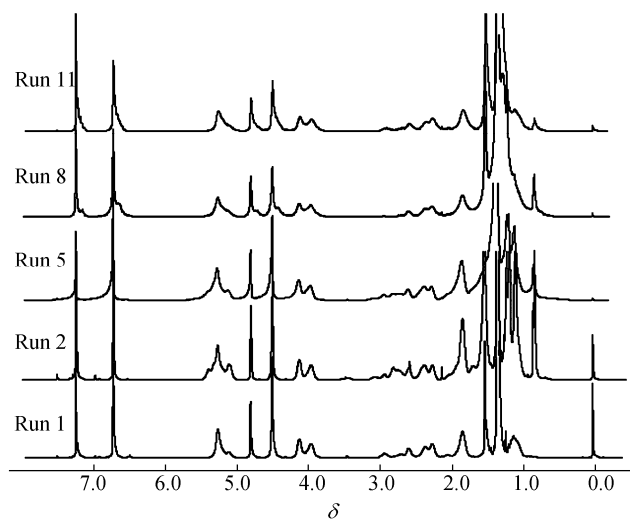


Fig. 1 ^1H -NMR spectra of polymer (Run 1) and copolymers (Run 2, 5, 8 and 11)

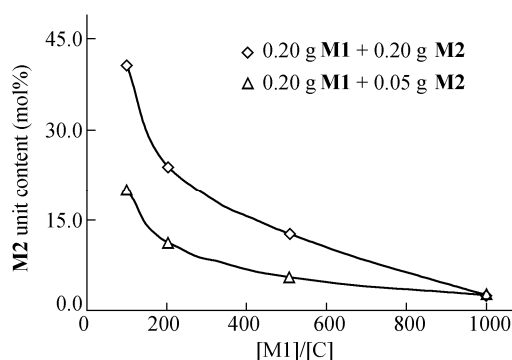


Fig. 2 The plot of **M2** unit content versus $[M1]/[C]$ ratio under the different **M2** feed

Figure 1 showed that olefinic proton signals of monomers were disappeared and new broad olefinic proton signals of polymer chain appeared at $\delta = 5.28$ and 5.10 which were assigned to *trans* and *cis* double bonds respectively. It was evidently demonstrated by *trans/cis* ratio that the resulting polymers contained predominantly *trans* structure in main chain. The stereochemistry of the polymers was determined by the steric factors from monomers' structure involved in the approach of the olefin to the Ru carbene. Because monomers **M1** and **M2** have bulky substituent, the relative ease of formation of the *trans* cyclometallabutane intermediate that determines *trans* double bonds is eventually formed during the propagation of the polymer chain initiated by $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$. In the case of polymer resulted from monomer **M1**, 86% of olefinic double bond in main chain was *trans* structure. Unfortunately, *trans/cis* ratio in copolymer could not be quantified due to indeterminable assignation of olefinic proton which appeared at the same displace with the $-\text{CH}-$ proton

signals of piperidine. Introducing **M2** units into copolymer chain gave rise to a degressive T_g . Copolymer (Run 2) containing 40.7% of **M2** units had a lower T_g (50.7°C) than the rest. Copolymers resulted from Run 3 and Run 5, likewise for copolymers resulted from Run 6 and Run 8, had a similar T_g corresponding to approximately equivalent **M2** unit content. And with the decrease of **M2** unit content, the T_g of copolymers increased to some extent. The **M2** unit content of copolymers resulted from Run 11, 12 was so low that no difference of T_g was observed, compared with T_g of **PM1** (Run 10).

CONCLUSIONS

Norbornene derivatives **M1** and **M2** bearing hindered phenol and hindered amine function group respectively were synthesized and copolymerized by sequential addition via ring opening metathesis polymerization (ROMP) using Grubbs 1st generation catalyst. A novel bi-functional polymer was prepared. The **M2** unit content in resulting copolymer could be regulated by **M2** feed and catalyst concentration. High **M2** feed was favorable to improving **M2** unit content, but high $[M1]/[C]$ ratio was not. The random copolymers resulted from chain transfer to polymer during the copolymerization. Due to the chain transfer reaction, chain scission occurred and M_n decreased to some extent. With regard to their performances and applications, it has to be studied rather critically.

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