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Synthesis and radical scavenging ability of new polymers from sterically hindered phenol functionalized norbornene monomers via ROMP

Boyong Xue, Kenichi Ogata, Akinori Toyota*

Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei-shi, Tokyo 184-8588, Japan

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Abstract

Norbornene derivatives, including four novel structure compounds, bearing sterically hindered phenol (SHP) were prepared as functional monomers (**1**–**3**). The ring-opening metathesis polymerization (ROMP) of these functional monomers was carried out with typical ruthenium catalyst [bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride] that was so called as first-generation Grubbs catalyst to prepare hindered phenol functionalized polymers possessing radical scavenging function. The resulting polymers were characterized by means of gel permeation chromatography (GPC), ^{1}H and ^{13}C NMR, and differential scanning calorimetry (DSC). The radical scavenging ability of polymer was evaluated by determining RSA using the α,α-diphenyl-β-picrylhydrazyl (DPPH) free radical. The results show that the resulting polymers have different radical scavenging ability with the difference in structure of side chain. Polymers bearing 3,5-di-*tert*-butyl-4-hydroxyphenyl-propionate (DBHP) side chain have a higher radical scavenging ability than the polymers bearing 3,5-di-*tert*-butyl-4-hydroxy-benzoate (DBHB) as side chain. The molecular weight of polymers is dependent on the ratio of molar concentration of monomer to catalyst ([M]/[C]); monomers bearing DBHP group have a higher activity for ROMP than the monomers bearing DBHB group comparatively.

Keywords: Ring-opening metathesis polymerization; Radical scavenging ability; Sterically hindered phenol

1. Introduction

Macromolecules endowed with radical scavenging ability constitute a unique and promising class of materials although there was limited information available in the literature regarding the homopolymerization of sterically hindered phenol functionalized monomers. Polymers falling within this category are suitable for polymeric stabilizers, self-stabilized materials and special scavenger resins that should be applied to biomedical materials and packing materials [1–4]. The general methods reported for preparing these polymers are grafting reaction [3–5], by which a sterically hindered phenol (SHP) group was bound into the polymer chain. These methods are normally associated with some problems, for example, part of SHP groups are consumed by the peroxide during grafting; the bulk polyolefin may undergo cross-linking and/or degradation and only a low level of binding is obtained as a result of major side reactions during the process; it is difficult to prepare polymer with controllable structure.

Ring-opening metathesis polymerization (ROMP) provides an attractive method for preparing functional polymers and copolymers as it is versatile, produces absolutely linear polymer and is amenable to form various copolymers with controlled architecture [6,7]. Well-defined ruthenium catalysts introduced by Grubbs and co-workers show high tolerance to a broad variety of functional groups on monomer unit and provide high level of control over polymer architecture [8–10]. Because of the strained nature of the norbornene ring, functionalized norbornene derivatives have been shown to be active monomers for ROMP [9,10]. Polymers bearing a variety of side chain have been prepared using various norbornene derivatives with different functional groups. Tlenkopatchev [11,12] synthesized one norbornene derivative 2-[(3,5-di-*tert*-butyl-4-hydroxybenzoyl)oxy]methyl-5-norbornene (**1a**) and polymerized

* Corresponding author. Tel./fax: +81 (0)42 388 7162.
E-mail address: a-toyota@cc.tuat.ac.jp (A. Toyota).

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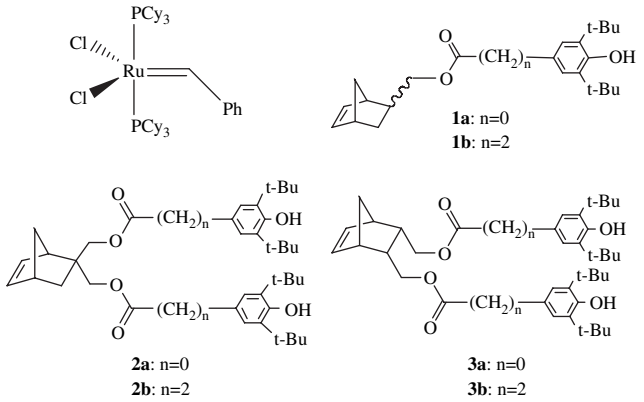


Fig. 1. Ruthenium catalyst and monomers (**1**–**3**) used in ROMP.

it via $RuCl_3$ and $OsCl_3$ as metathesis catalysts. This paper provided a way to improve oxidative stability of polynorbornene materials by incorporation of SHP into polymer main chain by metathesis polymerization for the first time, which could be regarded as a new route to self-stabilized polymers. The polymerization was carried out at high temperature, 70 °C for 24 h, and the molecular weight of polymer could be controlled by the molar ratio of monomer to catalyst. But about its performance related to antioxidation or radical scavenging should be investigated further. It would be a good way to obtain this kind of polymer with low PDI and controllable molecular weight under a mild reaction condition by using well characterized Ru catalyst. In general, functionalized olefinic monomers consist of functional unit and vinyl unit that are linked by some polar groups such as ester, ether, etc. Therefore, not only the choice of catalyst but also the design of monomer is key point for preparation of functionalized polymer. How to design and endow a monomer with suitable structure is a direct and effective way to improve polymerization activity and polymer's performance on the basis of commercial catalyst developed. In order to prepare this kind of functionalized polymers and uncover the relationship between monomer's structure and polymerization behavior, polymer's properties, various hindered phenol functionalized norbornene derivatives **1**–**3** were synthesized and polymerized by using ruthenium catalyst $RuCl_2(PCy_3)_2(=CHPh)$ as shown in Fig. 1. Herein, the polymerization behavior and the property of the resulting polymers will be reported in this paper.

2. Experimental

2.1. Materials

3,5-Di-*tert*-butyl-4-hydroxy-benzoic acid (98%), 5-norbornene-2-methanol (98%, mixture of *endo* and *exo*), 5-norbornene-2,2-dimethanol (98%), 5-norbornene-2-*endo*-3-*endo*-dimethanol (98%) and Grubbs first-generation catalyst ($RuCl_2(PCy_3)_2$-(=CHPh)) were purchased from Aldrich Chemicals and used without further purification. Diphenylpicrylhydrazyl (90%, Sigma); THF and pyridine (dehydrated, Wako) and dichloromethane (Kokusan Chemical Co.) were used after dehydrated. Methanol (spectroscopically pure, Kanto Chemical Co.); TLC aluminum sheets (Silica gel 60 F254, Merck); Silica Gel 60N (spherical, neutral, Kanto Chemical Co.). All other reagents and solvents were purchased from Tokyo Chemical Co., and used without further purification.

2.2. Monomer syntheses

The methods of synthesis of the monomers are disclosed below. All the processes were carried out in a nitrogen atmosphere. The yield was calculated after purification.

2.2.1. 2-[(3,5-Di-tert-butyl-4-hydroxybenzoyl)oxy]methyl-5-norbornene (*1a*)

This monomer containing DBHB group was prepared through 5-norbornene-2-methanol after acylation with 3,5-di-*tert*-butyl-4-hydroxy-benzoyl chloride (BHBC). The methods for preparing BHBC [13] and **1a** [11] were described in the literatures. Mp: 108 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.90 (s, 2H, Ar–H), 5.99–6.16 (m, 2H, –CH=CH–), 5.63 (s, 1H, –OH), 3.79–4.39 (m, 2H, $-CH_2OCO-$), 2.78–2.95 (m, 2H, –CH– in 1,4 position of norbornene ring), 2.53 (m, 1H, –CH– in 2 position of norbornene ring), 0.62–1.90 (m, 22H, *t*-Bu, $-CH_2-$).

2.2.2. 2,2-Bis[(3,5-di-tert-butyl-4-hydroxybenzoyl)oxy]-methyl-5-norbornene (*2a*)

5-Norbornene-2,2-dimethanol (3.0 g, 19.5 mmol) was dissolved in dichloromethane (60 ml). Pyridine 3.4 ml was added to above solution. The mixture solution was then stirred and cooled with ice bath at 0–5 °C. A solution of BHBC (12.0 g, 44.7 mmol) in 20 ml dichloromethane was added dropwise. The mixture was stirred for 24 h at room temperature and then filtered, washed with saturated sodium bicarbonate solution (50 ml) and distilled water (50 ml) three times. After drying with anhydrous magnesium sulfate, filtration, and removal of the solvent, a yellowish white product was collected. This product was purified by recrystallization two times from dichloromethane and dried in vacuum at 60 °C for 6 h (7.8 g, 65% yield). Mp: 205 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.87 (s, 4H, Ar–H), 6.21–6.24 (dd, 1H, ^3J 3 Hz, ^3J 3 Hz, olefinic proton in 6 position of norbornene ring), 6.11–6.14 (dd, 1H, ^3J 3 Hz, ^3J 3 Hz, olefin proton in 5 position of norbornene ring), 5.62 (s, 2H, –OH), 4.04–4.56 (m, 4H, $-CH_2OCO-$), 2.85–2.91 (m, 2H, –CH–), 1.00–1.72 (m, 40H, *t*-Bu, $-CH_2-$).

2.2.3. 2-endo-3-endo-Bis[(3,5-di-tert-butyl-4-hydroxy-benzoyl)oxy]methyl-5-norbornene (*3a*)

Monomer **3a** was prepared by using 5-norbornene-2-*endo*-3-*endo*-dimethanol as original reagent through the same synthesis process of **2b** (65% yield). Mp: 144 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 7.90 (s, 4H, Ar–H), 6.25 (s, 2H, –CH=CH–), 5.64 (s, 2H, –OH), 4.05–4.21 (m, 4H, $-CH_2OCO-$), 3.01 (s, 2H, –CH– in 1,4 position of norbornene ring), 2.72 (m, 2H, –CH– in 2,3 position of norbornene ring), 1.24–1.66 (m, 38H, *t*-Bu, $-CH_2-$).

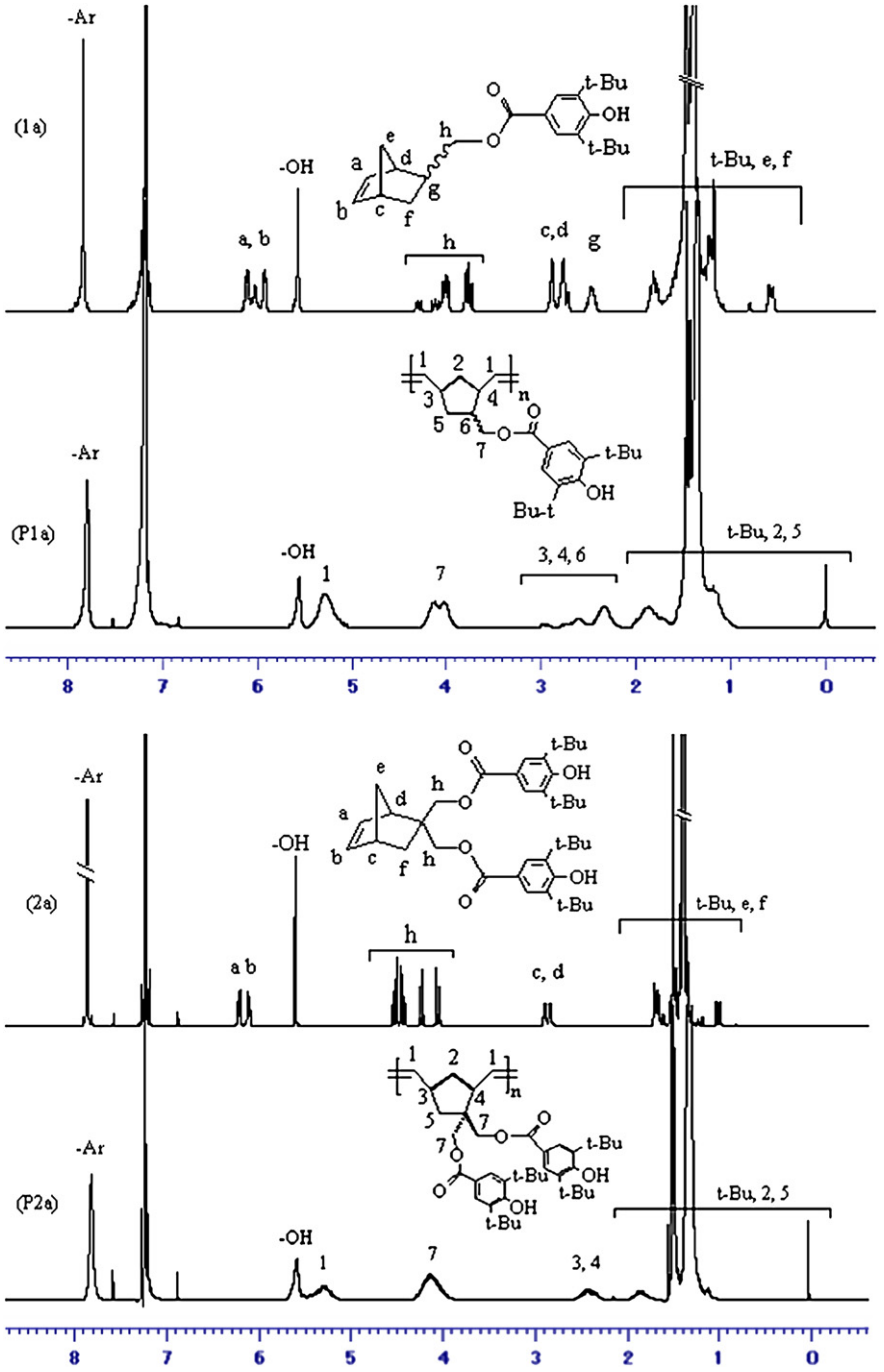


Fig. 2. ^{1}H NMR spectra of monomers and polymers (solvent: $CDCl_3$).

2.2.4. β-(3,5-Di-tert-butyl-4-hydroxyphenyl)propionic acid (3,5-PA)

A solution of β-(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl propionate (3,5-DBHMP) [14] (43.8 g, 0.15 mol) in 70 ml methanol was mixed with 22 ml sodium hydrate aqueous solution (30%). The mixture was heated to reflux for 2 h and allowed to cool. Aqueous HCl solution (6 N) was added dropwise until the pH value of mixture reached 1–3. A yellowish white product was colleted through filtration and dried in vacuum at 80 °C for 6 h (41.0 g, 98% yield). Mp: 175 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 6.98 (s, 2H, Ar–H), 5.06 (s, 1H, –OH), 2.83–2.89 (t, 2H, ^{3}J 9 Hz, $-CH_2COO-$), 2.56–2.61 (m, 2H, –CH2–), 1.41 (s, 18H, *t*-Bu).

2.2.5. β-(3,5-Di-tert-butyl-4-hydroxyphenyl)propionyl chloride (3,5-PC)

Thionyl chloride (5.3 ml) was added dropwise to a solution of 3,5-PA (10.0 g, 36 mmol) in 40 ml chloroform with stirring. The reaction mixture was heated to reflux for 6 h and allowed to cool. The solvent and the surplus thionyl chloride were removed under reduced pressure to give the crude product,

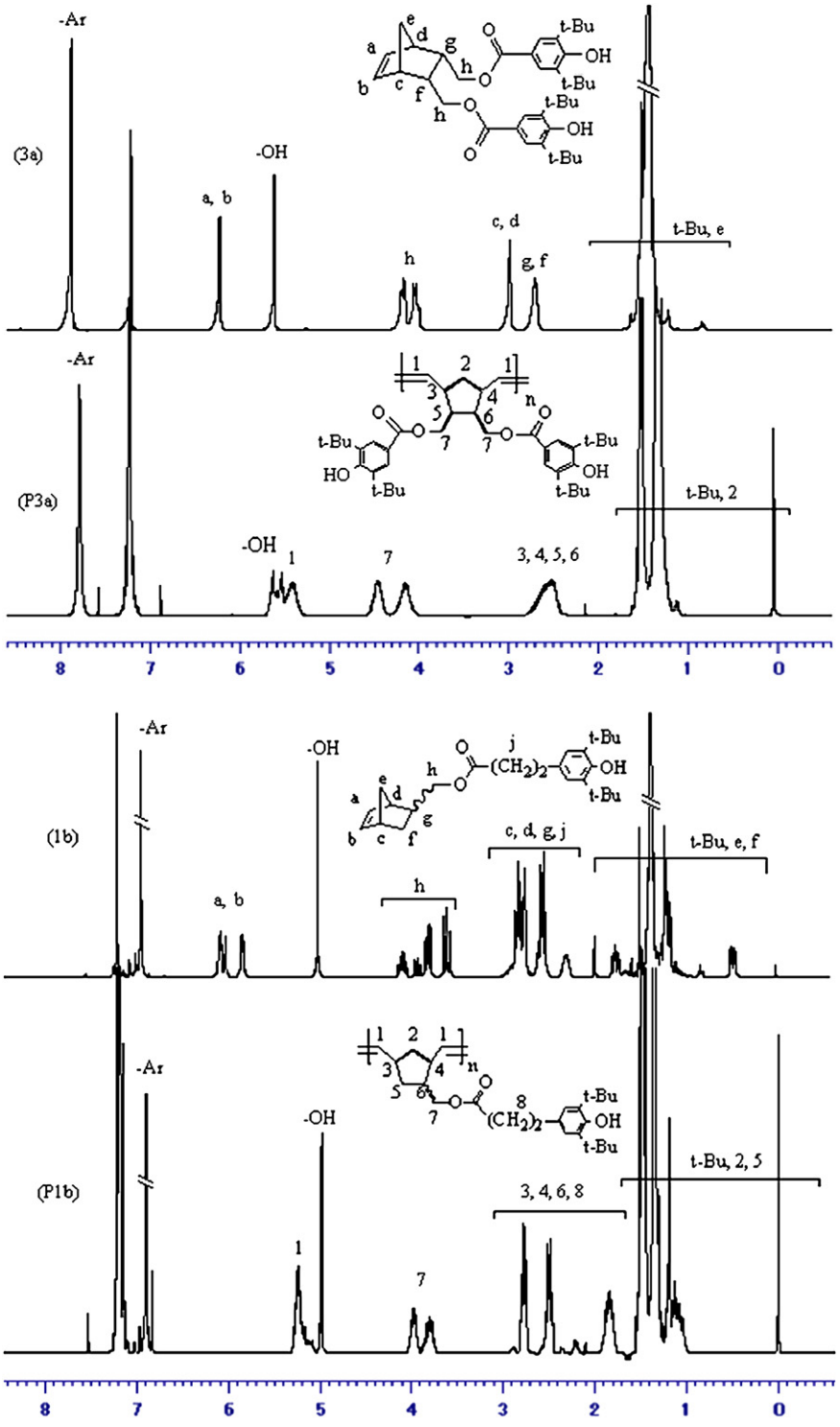


Fig. 2. (*continued*).

which was used without further purification for the next reaction.

2.2.6. 2-[3-(3,5-Di-tert-butyl-4-hydroxyphenyl)-propionyloxy]methyl-5-norbornene (*1b*)

Pyridine (2.7 ml) was added to a solution of 5-norbornene-2-methanol (4 g, 32 mmol) in 20 ml dichloromethane. The mixture was stirred and cooled in an ice bath at 0–5 °C. A solution of the above 3,5-PC in 20 ml dichloromethane was added dropwise. The mixture was stirred for 24 h at room temperature and then filtered and washed with saturated sodium bicarbonate solution (50 ml) and distilled water (50 ml) three times. After drying with anhydrous magnesium sulfate, the solution was filtered and removed under reduced pressure. The resulting yellow viscous oil was purified by column chromatography on silica gel with 1:3 (v:v) ethyl

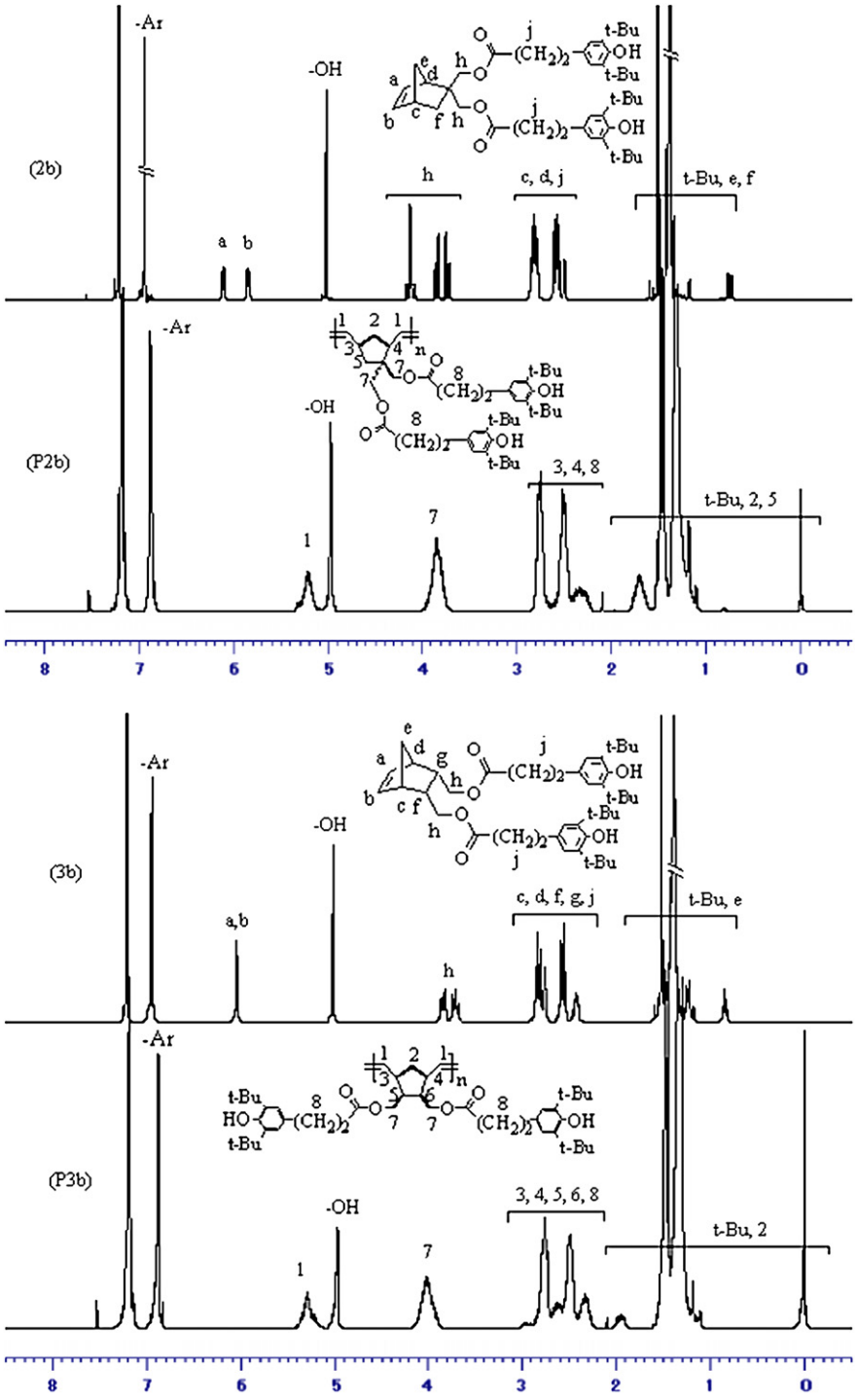


Fig. 2. (*continued*).

acetate/hexane as eluent ($R_f = 0.7$). In this way, the viscous and colorless liquid monomer **1b** (8.66 g, 68% yield) was obtained. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 6.98 (s, 2H, Ar−H), 5.83−6.16 (m, 2H, −CH═CH−), 5.07 (s, 1H, −OH), 3.56−4.16 (m, 2H, $-CH_2OCO-$), 2.28−2.93 (m, 7H, −CH− in 1,2,4 position of norbornene ring, $-CH_2-CH_2-$), 0.48−1.83 (m, 22H, *t*-Bu, $-CH_2-$ in 3,7 position of norbornene ring).

*2.2.7. 2,2-Bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionyloxy]methyl-5-norbornene (**2b**)*

Monomer **2b** was prepared from 5-norbornene-2,2-dimethanol (2.0 g, 13 mmol) in 60 ml dichloromethane by dropwise adding of the above 3,5-PC in 20 ml dichloromethane. Pyridine (2.2 ml) was used to remove HCl that was generated during the reaction. After a series of steps, also used in the synthesis process of **1b**, the resulting yellow viscous oil was

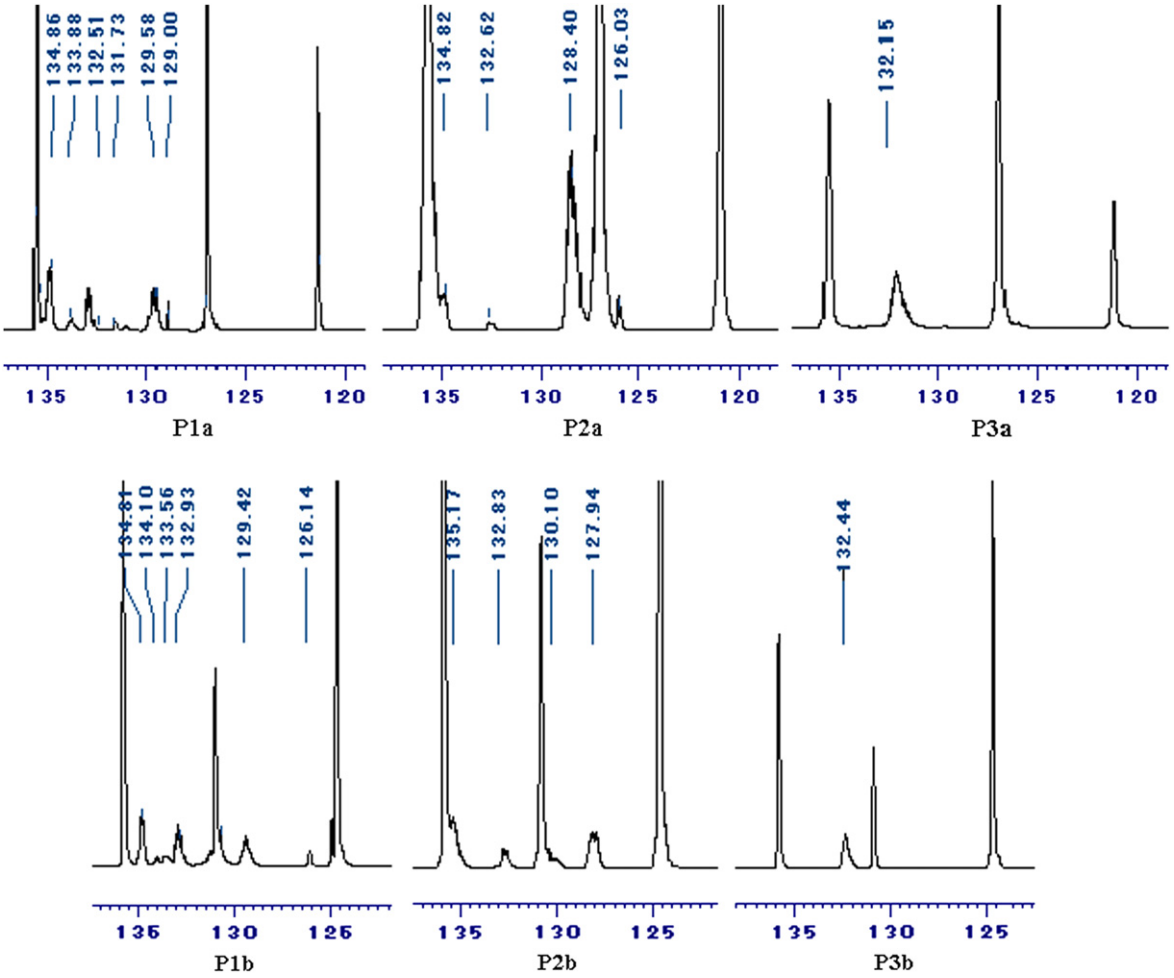


Fig. 3. ^{13}C NMR of polymers' olefin region (signals of phenyl, **P1b**–**3b**: $\delta = 135.89, 130.84, 124.64$; **P1a**–**3a**: $\delta = 135.59, 126.93, 121.36$).

purified by column chromatography on silica gel with 1:10 (v:v) ethyl acetate/hexane as eluent ($R_f = 0.4$). The resulting compound was then further purified by recrystallization from above-mentioned component solvent (6.12 g, 70% yield). Mp: 137 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 6.97 (s, 4H, Ar–H), 6.11–6.14 (dd, 1H, ^3J 3 Hz, ^3J 3 Hz, olefin proton in 6 position of norbornene ring), 5.85–5.88 (dd, 1H, ^3J 3 Hz, ^3J 3 Hz, olefin proton in 5 position of norbornene ring), 5.05 (s, 2H, –OH), 3.74–4.18 (m, 4H, $-CH_2OCO-$), 2.52–2.88 (m, 10H, –CH– in 1,4 position of norbornene ring, $-CH_2-CH_2-$), 0.74–1.62 (m, 40H, *t*-Bu, $-CH_2-$ in norbornene ring).

2.2.8. 2-endo-3-endo-Bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionyloxy]methyl-5-norbornene (*3b*)

Monomer **3b** was prepared from 5-norbornene-2-*endo*-3-*endo*-dimethanol (2.0 g, 13 mmol) by virtue of the same process as in Section 2.2.7. The resultant yellow viscous oil was purified by column chromatography on silica gel with 1:5 (v:v) ethyl acetate/hexane as eluent ($R_f = 0.45$). After further purification by recrystallization from ethyl acetate/hexane (1:10) component solvent, a white compound **3b** was obtained (3.26 g, 37% yield). Mp: 92 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, δ): 6.98 (s, 4H, Ar–H), 6.08 (s, 2H, –CH=CH–), 5.05 (s, 1H, –OH), 3.69–3.91 (m, 4H, $-CH_2OCO-$), 2.43–2.92 (m, 12H, –CH–, $-CH_2-CH_2-$), 0.84–1.62 (m, 40H, *t*-Bu, $-CH_2-$ in norbornene ring).

2.3. General polymerization procedure

The ROMP of monomers **1**–**3** gave polymers **P1**–**P3**. In a typical experiment, a 10-ml flask was charged with **1a** (200 mg, 0.56 mmol) in nitrogen atmosphere. CH_2Cl_2 (2.19 ml) and 0.91 ml catalyst dichloromethane solution (3 mmol/l) were added into the flask by syringe in sequence. The mixture was stirred at room temperature for 3 h. Polymerization was terminated by the addition of 0.3 ml of ethyl vinyl ether. After termination, the solution was stirred for an additional 10 min, and the polymer formed was precipitated in excess of methanol. The polymer was purified by reprecipitation from chloroform and methanol. The reprecipitated polymer was collected and then dried in vacuum for 12 h at room temperature to yield 193 mg **P1a** as a white solid (96.5% yield). The ^{1}H NMR is shown in Fig. 2 and ^{13}C NMR is shown in Fig. 3.

2.4. The evaluation of radical scavenging ability (RSA)

Resulting polymer (7 mg) was dissolved in 0.5 ml of chloroform to give a clear polymer solution; 0.1 ml of this solution was injected into quartz cell (1 cm × 1 cm) slowly by a syringe. The quartz cell with polymer solution at the bottom was put into a desiccator vertically and placed overnight under a nitrogen atmosphere to form a casting polymer film after chloroform solvent was evaporated naturally. α,α-Diphenyl-β-picrylhydrazyl (DPPH)/methanol solution (2 ml,0.1 mM/l) was injected into the quartz cell. After blown by some nitrogen, the cell was sealed up with a cap and covered with aluminum film, and then shaken (100 min^{-1}) for 3 h at room temperature. The radical scavenging ability (RSA) is defined in Eq. (1):

$$\mathrm{RSA}(\%) = \frac{A_0 - A_f}{A_0} \times 100\% - R_B \quad (1)$$

where A_0 is absorbance of the original DPPH solution; A_f is absorbance of the DPPH solution scavenged by casting film; R_B is the RSA value of blank sample. The absorbance of the DPPH solution was measured at 515 nm by ultraviolet–visible spectrophotometer. Compounds **1a** and 3,5-DBHMP were used as models . The RSA of them was defined by the same equation; 1.14 mg of model compound was dissolved in 50 ml of methanol to prepare 0.28 mg/ml solution. Model compound solution of 0.1 ml was injected into 2 ml of DPPH/methanol solution (0.1 mM/l) and then, this mixture solution was covered with aluminum film and shaken (100 min^{-1}) for 1 h, 2 h and 3 h at room temperature.

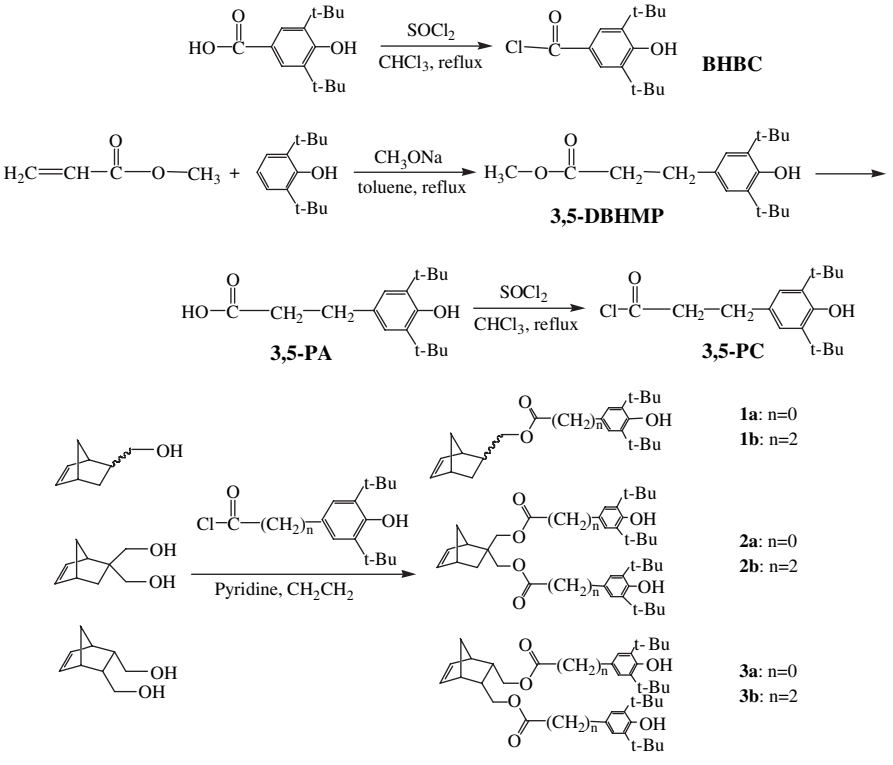
2.5. Characterization

The melting point of the compounds and the glass-transition temperature (T_g) of the polymers were determined in Shimadzu DSC-60 differential scanning calorimeter. A heating rate of 10 °C min^{-1} (0–200 °C) and nitrogen atmosphere was consistently employed. The ^1H NMR spectra were recorded on a JEOL JNM-AL300 NMR instrument at room temperature. The ^{13}C NMR spectra were recorded on a JEOL JNM-AL400 NMR instrument at room temperature. The molecular weight and molecular distribution of the polymers were determined with a JASCO gel permeation chromatography instrument equipped with a Shodex K-805L chromatograph column and a JASCO RI-2031 detector. The analysis was carried out at 40 °C with chloroform as eluent, at a flow rate of 1 ml min^{-1}. The molecular weights were calibrated with polystyrene standards. Visible absorption spectra were given by a JASCO UV-560 ultraviolet–visible spectrophotometer.

3. Results and discussion

3.1. Monomer synthesis and characterization

A series of monomers bearing SHP group were synthesized via the methods outlined in Scheme 1. Monomers **2a**, **2b**, **3a** and **3b** were formed by acylation reaction with an excess of BHBC or 3,5-PC in order to give disubstituted product as much as possible. There were two different SHP groups introduced in the monomers. One was 3,5-di-*tert*-butyl-4-hydroxybenzoate (DBHB) group, which was introduced in **1a**, **2a** and



Scheme 1. Synthesis of monomers **1**–**3**.

3a. The other was 3,5-di-*tert*-butyl-4-hydroxyphenyl-propionate (DBHP) group, which was introduced in **1b**, **2b** and **3b**. The structures of DBHB and DBHP in monomers were confirmed by ^{1}H NMR spectra (Fig. 2). The proton signals of aromatic hydrogens in DBHB appeared at 7.90 ppm, but those in DBHP appeared at 6.98 ppm as singlet. The structure difference between isomers **2a** and **3a** could be illuminated by the shift of the proton signals of olefinic hydrogens (H_a and H_b) clearly and simply. As to **2a**, the signals of H_a and H_b appeared in the range of 6.21–6.24 ppm and 6.11–6.14 ppm, respectively, as two batches of quartet. However, H_a and H_b, all of them in **3a** were shifted to the same displacement ($\delta = 6.25$) due to the symmetrical structure of **3a**. A similar shift phenomenon was observed in ^{1}H NMR spectra of isomers **2b** and **3b**, which also illuminated the structural difference between them. Two batches of signals in the range of 6.11–6.14 ppm (H_a) and 5.85–5.88 ppm (H_b) were shifted to the same displacement as $\delta = 6.08$.

3.2. Polymerization and characterization

ROMP, employing well-defined homogeneous catalyst systems, is an attractive method for preparing macromolecules. It provides broad flexibility over the choice of functional groups on the monomer unit and a high level of control over the macromolecular architecture. Compared with ^{1}H NMR of monomers and resulting polymers (Fig. 2), it can be easily found that the proton signals of olefinic hydrogens of each monomer disappeared and new broad olefinic proton signals of polymers appeared in the range of 5.30–5.35 ppm after polymerization and all of the resulting polymers contain predominantly *trans* double bound as main chain. The ^{13}C NMR of olefin region also supports that **1a**, **2a**, **1b** and **2b** give rise to polymers with head–head (HH), head–tail (HT, TH), and tail–tail (TT) dyads and **3a** and **3b** give rise to polymers with stereoregularity. For 5,5-disubstituted monomer **2b**, there were four olefinic signals assigned to the four types of carbon ($\delta_{TH} = 135.17$, $\delta_{TT} = 132.83$, $\delta_{HH} = 130.10$ and $\delta_{HT} = 127.94$) in **P2b**; likewise for **2a** ($\delta_{TH} = 134.82$, $\delta_{TT} = 132.62$, $\delta_{HH} = 128.40$ and $\delta_{HT} = 126.03$). Because **1a** and **1b** were mixture of *exo*- and *endo*- which lead to the formation of two different species during polymerization, ^{13}C NMR olefinic carbon of **P1a** and **P1b** was so complicated that the assignation of them was difficult. However, just like **2a** and **2b**, two isomers added randomly to the growing chain. Polymers will be stereoregular when made from 5,6-disubstituted monomers **3a** and **3b**, which was characterized by just one single ^{13}C NMR signal in olefin region of **P3a** ($\delta = 132.15$) and **P3b** ($\delta = 132.44$). But it was not sufficient to identify whether **P3a** and **P3b** were isotactic or syndiotactic. The regiochemistry and stereochemistry of the polymers were determined by the steric factors from monomer's structure involved in the approach of the olefin to the Ru carbine. Because monomers have bulky side substituent, the relative ease of formation of the intermediate *trans* metallacycles that determines *trans* double bonds is eventually formed during the propagation of the polymer chain. Initiated by this Ru catalyst, the ROMP of **1a**, **1b**, **2a** and **2b** was not provided with regionchemistry selectivity when monomer was linked to polymer chain.

All monomers **1**–**3** were subjected to ROMP using typical ruthenium catalyst $RuCl_2(PCy_3)_2(=CHPh)$ and the molar ratio of monomer [M] to catalyst [C] varied from 45 to 2966. The yield of polymer, number-average molecular weight (M_n), polydispersity index (PDI) and glass transition temperature (T_g) are summarized in Table 1. It can be seen that M_n increased with the increase of the value of [M]/[C], and the PDI value were in the range of 1.06–2.78. **P1a**, **P2a** and **P3a** bearing DBHB group as side chain have higher T_g than **P1b**, **P2b** and **P3b** that bear DBHP group as side chain, which could be attributed to the relative rigidity of the polymer side chain in the former three ones (no spacer between the carbonyl and phenyl in DBHB). T_g increased when polymer had two side chain in one unit of main chain. And T_g of **P3a** and **P3b** were about 5 °C and 1 °C higher than that of **P2a** and **P2b**, respectively, due to stereoregularity.

When [M]/[C] ratio was more than 205, **2a** could hardly be polymerized; likewise for **3a** when [M]/[C] ratio was more than 1000. But **1a**, **1b**, **2b** and **3b** could be polymerized in all ranges of [M]/[C] ratios from 205 to 2996. So **2a** and **3a** have lower activity for ROMP compared with other ones. **1b** was polymerized in 3.1 ml and 10.0 ml of solvent respectively. Initiated in 3.1 ml solvent, the mixture of the runs 12–14 became too viscous to be stirred normally in 15 min. And molecular weight was so high that the resulting polymer could

Table 1
ROMP of substituted norbornene monomers

Run	Monomer	[M]/[C][a]	Yield (%)	$M_n/10^4$	$M_{th}/10^4$	PDI	T_g (°C)
1	**1a**	205	96.5	8.0856	7.0527	1.19	135.58
2	**1a**	1000	98.8	39.4659	35.2232	1.25	135.61
3	**1a**	2000	99.1	72.1016	70.6603	1.42	135.86
4	**1a**	2800	94.6	91.2492	94.4324	1.61	135.56
5	**2a**	45	71.0	2.5956	1.9772	1.08	165.32
6	**2a**	100	76.7	6.3147	4.7466	1.19	165.34
7	**2a**	205	Trace	–		–	–
8	**3a**	45	76.8	3.3740	2.1387	1.10	166.48
9	**3a**	205	37.9	8.0268	4.8082	1.20	166.64
10	**3a**	1000	Trace	–	–	–	–
11	**1b**	205	97.4	14.3860	7.6785	1.97	70.68
12	**1b**	1000	99.8	Insoluble	–	–	73.24
13	**1b**	2000	99.7	Insoluble	–	–	73.56
14	**1b**	2889	99.8	Insoluble	–	–	73.26
12[b]	**1b**	1000	86.5	50.5196	33.2644	2.78	72.75
13[b]	**1b**	2000	80.5	82.8096	61.8757	2.60	72.63
14[b]	**1b**	2889	80.9	102.2548	89.8239	1.81	73.12
15	**2b**	205	78.7	8.4863	10.8774	1.14	75.41
16	**2b**	1000	27.4	16.6642	18.4734	1.13	75.36
17	**2b**	2000	14.6	17.7672	19.6869	1.12	75.57
18	**2b**	2966	12.5	25.3235	24.9963	1.06	75.33
19	**3b**	205	80.4	8.5762	11.1123	2.39	80.27
20	**3b**	1000	53.8	32.1202	36.2725	1.37	80.40
21	**3b**	2000	34.5	42.9260	46.5205	1.52	80.33
22	**3b**	2966	28.0	59.1171	55.9918	1.28	80.76

Polymerization conditions: 200 mg of monomer; methylene chloride was used as solvent; total volume of solvent was 3.1 ml; polymerization for 3 h; room temperature; the reaction was terminated by 0.3 ml of ethyl vinyl ether.

[a] [Monomer]/[catalyst].

[b] Total volume of solvent was 10 ml. M_{th}: theoretical value of molecular weight.

not be dissolved. The propagation rate constant k_p of **1b** is greater than the initiation rate constant k_i to such an extent that carbine complexes not fully consumed before the monomer has been completely polymerized [9], which makes **P1b** have very high M_n in a shorter time and broad PDI. The yield and molecular weight of **P1b** decreased when the mixture of the runs 12^b–14^b was initiated in 10 ml solvent, which can be contributed to the concentration effect of the monomer. **P2a**, **P3a** and **P2b** had low PDI (<1.2) and M_ns close to theoretical ones which indicated a living polymerization of **2a**, **3a** and **2b**. The increase of PDI, resulting from the increase of k_p/k_i, indicated that **1b**, **1a** and **3b** had higher propagation rate comparatively and there were back-biting or cross-linking reaction during the propagation of living chains. Compounds **2a** and **3a** had such a low propagation rate that the growth of polymer chain hardly proceed when [M]/[C] was more than 205 and 1000 within 3 h.

According to the results shown in Table 1 and Fig. 4, it can be seen that M_n and yield of **P3b** were higher evidently than those of **P2b** under the same [M]/[C] and reaction time; likewise for **P3a** and **P2a**. In other words, catalyzed by $RuCl_2(PCy_3)_2$(=CHPh), **3b** has higher activity for ROMP than **2b** and **3a** has higher activity for ROMP than **2a**. Analogically, the order **1b** > **1a** > **3b** > **2b** > **3a** > **2a** for ROMP activity could be found according to comparison of M_n and yield. These interesting results can be primarily attributed to the electron density of carbonyl oxygen atom in the DBHB group is higher than that in the DBHP group, which could be illustrated by mechanism analysis of propagating living chain of **P3a** and **P3b** as an example in the following discussion (Scheme 2). Haigh [15,16] studied the nature of the propagating species in ROMP of oxygen-containing norbornene derivatives and identified unambiguously that besides bisphosphine species (I, Scheme 2), an additional monophosphine propagating species (II, Scheme 2) in which oxygen in the propagating polymer backbone chelating to the Ru center will be formed when norbornene monomers containing oxygen are subjected to ROMP initiated by $RuCl_2(PCy_3)_2$(=CHPh). According to the mechanism of metathesis reactions catalyzed by $RuCl_2(PCy_3)_2$(=CHPh) [17,18], the crucial step is disassociation

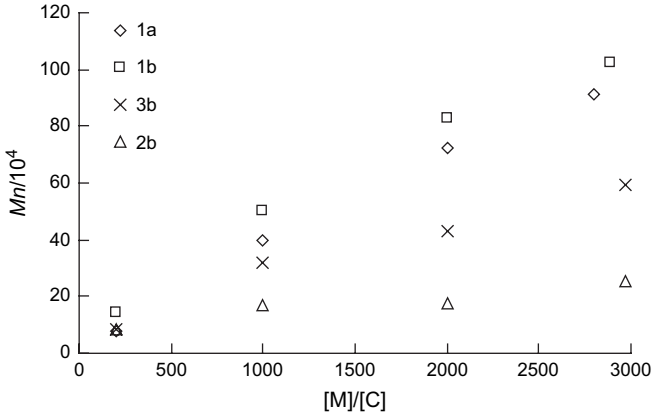
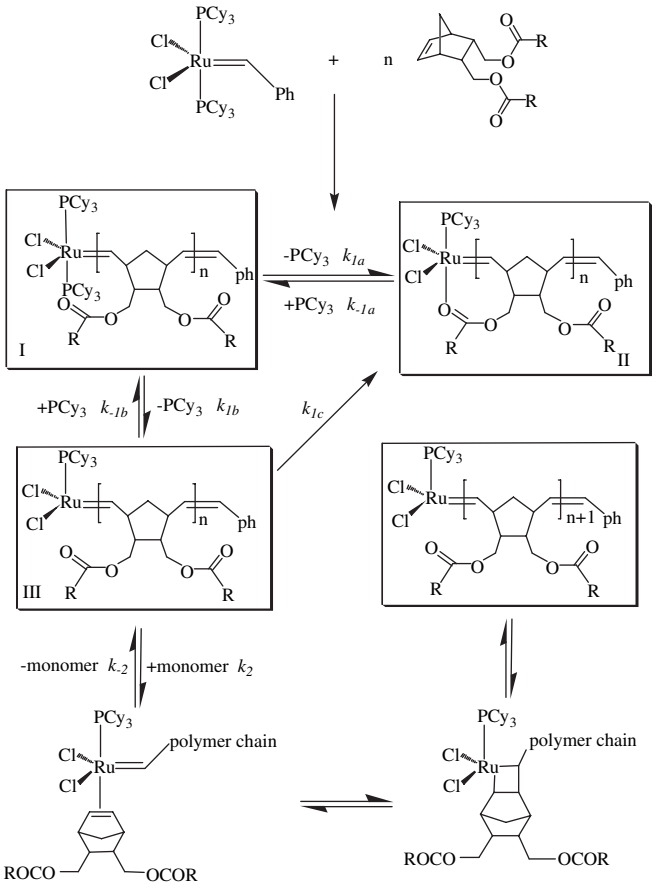
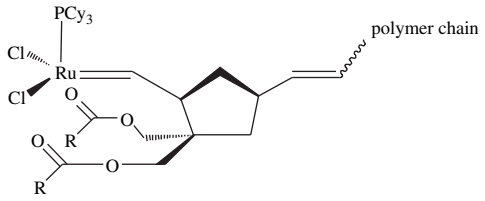


Fig. 4. Plot of number of average molecular weight (M_n) versus [M]/[C] ratio (**1b** was polymerized in 10 ml solvent when [M]/[C] was 1000, 2000 and 2889).



Scheme 2. Propagating living chain of **P3a** and **P3b** in ROMP (**P3a**: R = −SHP, **P3b**: R = $(CH_2)_2$−SHP).

of bound PCy_3 to form an intermediate of the species III (k_{1b}). This intermediate species III can be trapped by free PCy_3 to regenerate the starting species I (k_{-1b}) or can bind monomer and undergo metathesis (k_2), and it is also possible for species III to transform to species II through k_{1c}. Due to the fact that **3a** and **3b** have the same strained norbornene ring and are initiated by the same catalyst, k_{1b} and k_2 of **3a** are equal to those of **3b**. An irreversible conversion (k_{1c}) and a reversible conversion (k_{1a}/k_{-1a}) between I and II exist at the expense of the reaction k_{1b} and k_2, and then has a great influence on the rate of propagating polymer chain (k_p). Therefore, the activity of **3a** and **3b** for ROMP is dependent on the ratio of $k_{1b}/(k_{1a}\cdot k_{1c})$. Because of electron-withdrawing inductive effect (−I) and electron-withdrawing conjugation (−C) of carbonyl group substituted on the phenyl, the electron density of carbonyl oxygen in DBHB is enhanced, but the electronic nature of carbonyl oxygen in DBHP is not changed due to the presence of an ethylidene group that interrupts the −I and −C effects of the carbonyl. Consequently, oxygen in the propagating polymer backbone of **P3a** is able to chelate to the Ru more easily and form more stable species II in comparison with oxygen in the propagating polymer backbone of **P3b**, which means $k_{1a}\cdot k_{1c}$ of **3a** is higher than that of **3b**. As a result, **3b** have higher activity for ROMP than **3a**. The same presume also applies to another two groups of monomers **1** and **2**. Moreover, the activity of monomers for ROMP also



Scheme 3. Propagating species of **P2a** or **P2b** in ROMP (**P2a**: R = −SHP, **P2b**: R = $(CH_2)_2$−SHP).

has relation to the amount and the position of oxygen-containing substituent closely. The probability of oxygen in the propagating polymer backbone chelating to the Ru center is increased with increasing amount of substituting groups and increased more largely when two substituting groups are situated on the two sides of ring (Scheme 3). According to this presumption, disubstituted monomers **2a**, **2b**, **3a** and **3b** have lower activity for ROMP than singly substituted **1b** and **1a**; as to **2a** and **2b**, the two substituting groups are situated on the two sides of ring, which makes each of them have lower activity for ROMP than **3a** and **3b**, respectively.

3.3. Radical scavenging ability

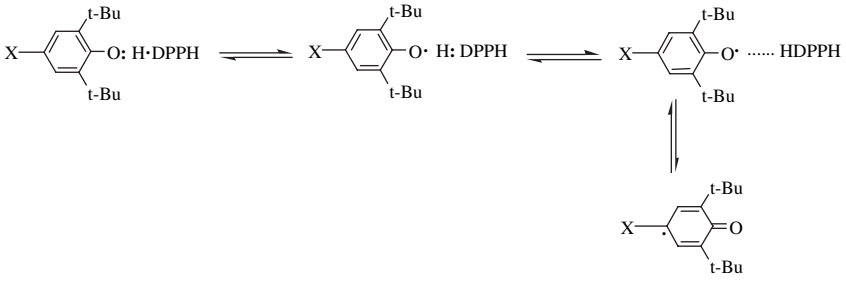
Radical scavenging abilities of resulting polymers were assessed on the basis of the capacity of the polymer films to scavenge the stable α,α-diphenyl-β-picrylhydrazyl (DPPH) free radical, a procedure widely used to test the antioxidant properties of SHP molecules. It could be proposed that the radical scavenging activity values obtained by the DPPH method make it possible to predict the activity of resulting polymers in other antioxidation systems [19,20]. A methanol solution of DPPH• has maximum absorption peak at 515 nm. This absorption was seen to decline after the methanol solution of DPPH• was shaken in the presence of the films of the resulting polymers. A SHP works as a radical scavenger by hydrogen transfer from the phenol to DPPH• during the reaction (Scheme 4). The radical scavenging ability of the resulting polymers is compared in Table 2. The RSA of **P2a** and **P3a** is higher than that of **P1a** due to the fact that there are more SHP groups in **P2a** and **P3a** under the same weight. The same result will also apply to **P2b**, **P3b** and **P1b**. The possible reason why the RSA of **P2b** and **P3b** was not double as that of **P1b** was that the radical scavenging reaction proceeded with a nonlinear relationship to the concentration of SHP. Polymers **P1b**, **P2b** and **P3b** bearing DBHP groups as side chain have a higher

Table 2
Radical scavenging ability of the polymers and model compounds

Polymer	RSA (%)
P1a	10.44
P2a	17.56
P3a	18.48
P1b	33.37
P2b	43.41
P3b	42.92
3,5-DBHMP	48.78[a], 57.32[b], 61.35[c]
1a	5.95[a], 7.04[b], 7.22[c]

[a] Shaken for 1 h.
[b] Shaken for 2 h.
[c] Shaken for 3 h.

radical scavenging ability than the polymers **P1a**, **P2a** and **P3a** bearing DBHB groups as side chain evidently, which can be attributed to the effect of *para*-substituent of phenol is different between DBHP and DBHB. To support this conclusion, RSA of **1a** and 3,5-DBHMP were assessed too (Table 2). It could be evidently found that 3,5-DBHMP had higher RSA than **1a**; RSA increased prominently within the first two hours. Ingold and Howard [21,22] studied the antioxidant activity of phenol on the basis of the inhibition reaction of peroxy radical with phenol and gave a clear opinion on the substituent effects. It has been reported that the logarithm of the inhibition rate constant (k_{inh}) is well correlated with the total value of electrophilic substituent constants (σ^+) on both *ortho*- and *para*-positions. The relationship between k_{inh} and σ^+ of substituents of phenol could be expressed as: $\log k_{inh} = \alpha + \rho \sum \sigma^+$, which means that radical inhibition activity (k_{inh}) of a phenol is increased when substituents have higher electron-donating property such as *tert*-butyl. This conclusion was verified and developed further by Ohkatsu [23,24] in recent years. Because the electronic effect of group situated in the *para*-position of phenol is different, phenolic oxygen in DBHP has higher electron density than that in DBHB. A DPPH• approaches the electron-rich phenolic oxygen in an electrophilic manner and abstracts the electron, then the resulting carbanion-like DPPH• radical abstracts the phenolic hydrogen as a proton. DBHP phenolic oxygen is attacked more easily by DPPH• because of higher electron density. On the other hand, the hydrogen abstraction reaction is reversible. The ethylidene in DBHP makes the resulting DPPHH leave easily due to localization of the radical on *para*-position and consequently increase the RSA further.



Scheme 4. Scavenging mechanism of DPPH radical.

4. Conclusions

In conclusion, six kinds of norbornene derivatives, including four novel structure compounds, bearing sterically hindered phenol groups were synthesized and polymerized via ROMP by using $RuCl_2(PCy_3)_2(=CHPh)$ as catalyst. The structure of monomers and polymers could be successfully explained by ^1H and ^{13}C NMR spectra. The molecular weight of polymers is dependent on the ratio of molar concentration of monomer to catalyst ([M]/[C]). Monomers bearing DBHP groups have higher activity for ROMP than monomers bearing DBHB groups comparatively. The radical scavenging ability of the resulting polymers was evaluated by determining radical scavenging ability using the DPPH free radical. The polymers **P1b–P3b** bearing DBHP side chain have a higher radical scavenging ability than the polymers **P1a–P3a** bearing DBHB as side chain. Thus, all of the results throw light on the design and synthesis of highly effective radical scavenging polymer. An effective method for improving monomers ROMP activity is to make norbornene-based monomers have single substituent and low electronegative polar group as link spacer. It may be regarded as one of the principles for the rational design of functionalized norbornene-based monomers.

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