

# Synthesis and characterization of block copolymer with pendant carbazole group via living ring-opening metathesis polymerization

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## Abstract

A new carbazole-functionalized norbornene derivative, 5-(*N*-carbazolyl methylene)-2-norbornene (CbzNB), was polymerized via living ring-opening metathesis polymerization with  $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$ . The structure of the poly(CbzNB) was analyzed by NMR, IR and fluorescence spectroscopy. The resulting polymer was of high molecular weight and had a reasonably narrow molecular weight distribution ( $\bar{M}_n = 320\,000$ , PDI = 1.28). Block copolymer of the CbzNB and a trimethylsilyl-protected alcohol-functionalized norbornene derivative was also synthesized by ROMP techniques. Glass transition temperature ( $T_g$ ) of poly(CbzNB) is  $160^\circ\text{C}$ . The 10% decomposition temperature of poly(CbzNB) is  $410^\circ\text{C}$ . Saturation of the main-chain double bonds of poly(CbzNB) increases the thermal stability of the polymer but decreases the  $T_g$  of polymer. Microphase separation and selective reaction of the alcohol-functionalized domains with dimethyl cadmium were observed by transmission electron microscopy. © 2000 Elsevier Science Ltd. All rights reserved.

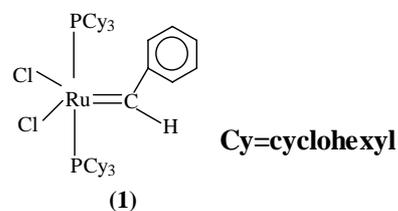
**Keywords:** Living ring-opening metathesis polymerization; Block copolymer; Carbazole

## 1. Introduction

Increasing interest in ring-opening metathesis polymerization (ROMP) of norbornene derivative containing functional groups has developed over the recent years, aiming to obtain polymer structures with reactive substituents having attractive properties [1,2]. Carbazolyl-substituted polymers are well known as precursors for the electrophotographical materials with valuable optical, photoconductive and other useful applications such as organic light emitting diodes [3]. Since the first application of poly(*N*-vinylcarbazole) in xerography [4], great interest has been focused on photoconductivity and electrochemical property of carbazole-containing polymers [5–8].

Carbazole-functionalized norbornene derivatives have been polymerized recently using classical, nonliving olefin metathesis catalysts such as  $\text{RuCl}_3$  and  $\text{RuCl}_2(\text{PPh}_3)_3$  [1,9]. The resulting homopolymer was reported to exhibit interesting properties, but the control over molecular weight and molecular weight distribution was poor, and block copolymers could not be obtained. Cohen et al. [10] reported the living ring-opening metathesis polymerization (ROMP) of 5-methyl[bis(*N*-carbazolyl)silyl]-2-norbornene

with a well-defined ruthenium complex (1) described by Grubbs et al. [11,12].



In view of the limited information available in the literature regarding the ROMP of carbazole-functionalized norbornene derivatives, in this work, low-polydisperse new homopolymers of a carbazole-functionalized norbornene derivative [5-(*N*-carbazoyl methylene)-2-norbornene] (CbzNB) were prepared. Block copolymer of 5-(*N*-carbazoyl methylene)-2-norbornene and 5-[(trimethylsilyloxy)methylene]-2-norbornene were also prepared, and the polymers were hydrolyzed to remove the protecting group. These new materials are of special interest. Several studies have reported that microphase-separated block copolymers with hydroxyl functional groups are useful templates in the synthesis of semiconducting metal sulfide nanoclusters [13–15]. Thus, with the development of a carbazole functionalized block copolymer, the resulting

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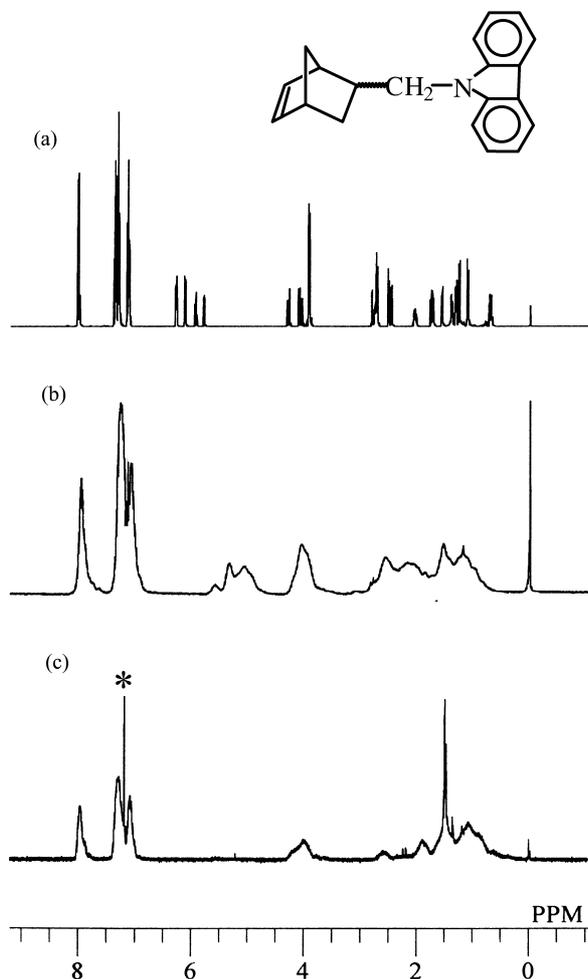


Fig. 1. 400 MHz <sup>1</sup>H NMR spectra taken in CDCl<sub>3</sub> at 25°C: (a) CbzNB monomer; (b) CbzNB homopolymer; (c) hydrogenated poly(CbzNB), \* solvent peak.

materials are expected to exhibit novel optoelectronic properties that should be of use in a variety of practical applications.

This article describes the synthesis of new carbazolyl-substituted norbornene, containing both carbazole and norbornene units. It is used to prepare polymers with various molecular weights via living ROMP. Block copolymers of the CbzNB and a trimethylsilyl-protected alcohol-functionalized norbornene derivative were prepared. Synthesis and characterization of these poly(CbzNB)s and block copolymers are also investigated and discussed.

## 2. Experimental

### 2.1. Materials

All the chemicals were used as received without purification unless otherwise mentioned. Carbazole was purchased from Riedel-de Haen (Germany). Bis(tricyclohexylphosphine)-benzylideneruthenium dichloride (complex 1)

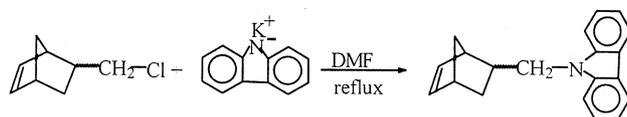
was purchased from Strem. Dicyclopentadiene was purchased from Merck. Allyl chloride, allyl alcohol, *p*-toluenesulfonylhydrazide, cadmium iodide, iodomethane, naphthalene and sodium were purchased from Acros. Solvents such as xylene, tetrahydrofuran (THF) and dimethylformamide (DMF) were purified by normal procedures and handled under moisture-free atmosphere. The polymerization solvent methylene chloride was dried over calcium hydride and distilled before use. The synthesis of 2-chloromethylene-5-norbornene (bp = 54–56°C/11 mmHg) and 2-norbornene-5-methanol (bp = 92–95°C/13 mmHg) was accomplished via the Diels–Alder condensation of freshly cracked cyclopentadiene and the corresponding allyl chloride and allyl alcohol, respectively [16]. Dimethyl cadmium was prepared by the reaction of highly active cadmium metal and iodomethane [17]. The highly active cadmium metal was prepared by the reaction of sodium/naphthalene with cadmium iodide in THF. That is, sodium (4.1 g, 0.17 mol) and naphthalene (2.4 g, 0.017 mol) in 70 ml of anhydrous THF was treated with cadmium iodide (32 g, 0.087 mol) over 30 min at room temperature. The mixture was stirred for an additional 2 h. The above mixture yielded a highly active cadmium metal which was stirred continuously with iodomethane (21.6 g, 0.15 mol) at 40°C for 3 h to give dimethyl cadmium.

### 2.2. Monomer synthesis

#### 2.2.1. 5-(*N*-Carbazoyl methylene)-2-norbornene

The potassium salt of carbazole was prepared by azotropic removal of water from an equimolar solution of potassium hydroxide (12 g) and carbazole (30 g, 0.183 mol) in xylene (200 ml) [18]. The solvent xylene was removed and replaced by DMF. 5-Chloromethylene-2-norbornene (25 g, 0.178 mol) was added to the potassium salt of carbazole in DMF which was then refluxed for 12 h. The solution was poured into water (200 ml) and extracted three times with ethyl acetate (100 ml, each). After the solvent was removed with an evaporator, the residue was purified using silica-gel column chromatography [9] (eluent; ethyl acetate:*n*-hexane, 1:6) and by recrystallization from *n*-hexane, mp = 74–76°C [endo/exo = 3 : 2, <sup>1</sup>H NMR (CDCl<sub>3</sub>), Fig. 1(a), 6.15 (m, =CH, endo), 6.06 (m, =CH, endo), 5.95 (m, =CH, exo), 7.75, 7.60 (m, 4H, aromatic)].

The monomer was sufficiently pure for polymerization. The reaction is shown below.



<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ (ppm) 140.4, 138.3, 136.5, 136.1, 132.4, 125.5, 122.7, 120.1, 118.6, 108.8, 50.0, 48.1, 47.0, 45.0, 44.5, 44.0, 42.6, 41.8, 39.0, 38.6, 30.8, 30.5.

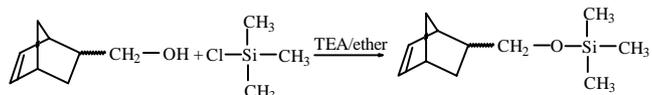
IR (KBr pellet,  $\text{cm}^{-1}$ ); 1587( $\nu_{\text{C}=\text{C}}$ , vinylic), 1647, 1478( $\nu_{\text{C}=\text{C}}$ , aromatic stretching), 1324( $\nu_{\text{C}-\text{N}}$ ), 745, 718( $\nu_{\text{C}-\text{H}}$ , carbazole ring out-of-plane).

UV(THF):  $\lambda_{\text{max}} = 236.2 \text{ nm}$ ,  $\epsilon = 4.19 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ .

Elemental analysis: ( $\text{C}_{20}\text{H}_{19}\text{N}$ ). Calculated: C: 87.87%, H: 7.01%, N: 5.12%. Found: C: 87.58%, H: 7.08%, N: 5.31%.

### 2.2.2. 5-[(Trimethylsiloxy) methylene]-2-norbornene

5-[(Trimethylsiloxy) methylene]-2-norbornene was prepared from the reaction of 2-norbornene-5-methanol with trimethylchlorosilane and triethylamine in diethyl ether [19]. The product was obtained as colorless oil after distillation under vacuum. (44–46°C/2 mmHg) [endo/exo = 9 : 1,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ), 6.15 (m, =CH, endo), 6.06 (m, =CH, endo), 5.95 (m, =CH, exo), 7.75, 7.60 (m, 4H, aromatic)]. The reaction is shown below:



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ (ppm) 136.8, 136.4, 136.3, 132.1, 66.9, 66.1, 65.9, 49.4, 44.7, 43.6, 43.3, 42.2, 41.7, 41.5, 29.5, 28.9, 0.1. IR (KBr pellet,  $\text{cm}^{-1}$ ); 1618( $\nu_{\text{C}=\text{C}}$ , vinylic), 878( $\nu_{\text{Si}-\text{O}}$ ).

## 2.3. Polymerization

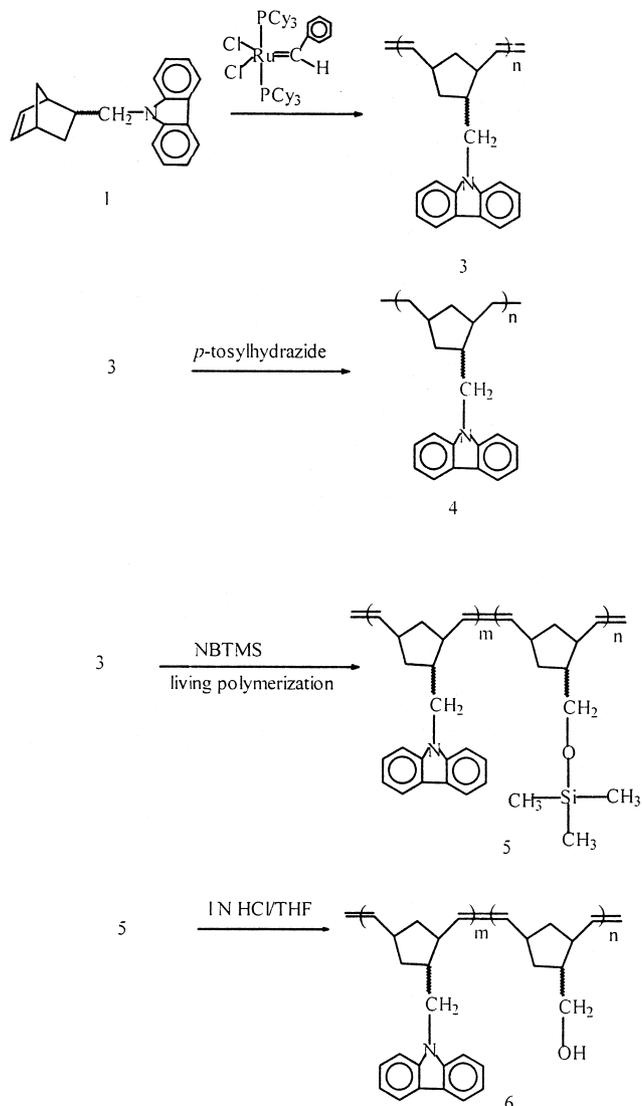
### 2.3.1. Ring-opening metathesis polymerization of CbzNB

The ring-opening metathesis polymerization of CbzNB was carried out by metathesis catalyst  $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$ , under oxygen free condition. A typical procedure is as follows: a solution of catalyst was prepared by dissolving  $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$  (0.5 mg,  $6 \times 10^{-4}$  mmol) in 1 ml of anhydrous methylene chloride under an argon-filled dry box. The monomer CbzNB (0.2 g, 0.73 mmol) was dissolved in 2 ml of methylene chloride and then degassed via a freeze-pump-thaw cycle. After it was degassed completely, the catalyst solution was injected into the monomer solution by syringe. The reaction was carried out at 25°C for 1 h. (An analysis of reaction mixture by GPC revealed that the polymerization was essentially completed in 1 h.) The color of the solution changed from pink to yellow when the reaction was carried out at 25°C for 10 min. To obtain homopolymer, the reaction was terminated by the addition of a small amount of ethyl vinyl ether (0.2 ml). The polymer was then precipitated in excess methanol (300 ml). The white polymer was further purified by dissolving it in methylene chloride and re-precipitating it with methanol and drying it overnight in a vacuum at room temperature. Yield = 97%. ( $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ , Figure 1 (b)).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 140.2, 133.7, 132.1, 125.3, 122.6, 120.2, 118.6, 108.8, 48.4, 45.4, 44.5, 42.8, 41.8, 36.3.

### 2.3.2. Block copolymer of 5-(N-Carbazoyl methylene)-2-norbornene and 5-[(trimethylsiloxy) methylene]-2-norbornene

To obtain block copolymer, monomer 5-[(trimethylsiloxy) methylene]-2-norbornene (0.17 g, 0.73 mmol) was injected into the still-living reaction mixture and the solution was stirred continuously for another 1 h before termination as described above. The polymer was precipitated in methanol. The precipitated polymer was again dissolved in tetrahydrofuran and re-precipitated in methanol, filtered and dried under vacuum at room temperature.  $\bar{M}_n = 110000$  and PDI = 1.25 by GPC. ( $^1\text{H}$  NMR, 400 MHz,  $\text{THF-d}_8$ , Fig. 4 (a)).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 141.2, 135.5, 130.7, 126.0, 123.7, 120.7, 119.2, 109.7, 46.0, 45.9, 43.5, 41.0, 37.6, 32.7, 1.4.

Block copolymer 5 (Scheme 1) was hydrolyzed by adding 15 ml of tetrahydrofuran and 1 ml of 1 N HCl (aq.) to 0.2 g of copolymer 5 and allowing the mixture to stand at room



Scheme 1.

temperature for 3 h, when a complete solution had almost been achieved. The polymer was then precipitated in excess methanol (300 ml) and dried overnight in a vacuum oven at room temperature. Yield = 95%.  $\bar{M}_n = 95\,000$  and PDI = 1.32 by GPC. ( $^1\text{H}$  NMR, 400 MHz, THF- $d_8$ , Fig. 4(b)).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 141.2, 134.4, 131.2, 125.9, 123.5, 120.6, 119.1, 109.6, 48.8, 46.2, 45.6, 43.5, 40.9, 37.9.

### 2.3.3. Hydrogenation of poly(CbzNB)

In a typical experiment [20], 0.2 g of poly(CbzNB) was dissolved in 20 ml of xylene in an ampoule. To the above solution was added 1.0 g (7.3 equiv. relative to the repeating unit) of *p*-toluenesulfonylhydrazide as a hydrogenation agent and a trace amount of 2,6-di-*tert*-butyl-4-methylphenol. The ampoule containing the polymer, solvent and hydrogenation agent was then degassed three times via a freeze–pump–thaw cycle and sealed. The ampoule was heated to 120°C. At 100°C, a homogeneous solution resulted and nitrogen started to evolve. The solution was stirred at 120°C for 3 h until the evolution of nitrogen stopped. The solution was cooled to room temperature and precipitated from methanol. The white polymer was further purified by dissolving it in methylene chloride and re-precipitating it with methanol. The polymer was dried in vacuo overnight at room temperature. Yield = 0.18 g (90%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , Fig. 1(c)).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm) 140.5, 125.4, 122.7, 120.2, 118.6, 108.9, 44.8, 43.9, 40.9, 38.8, 38.5, 36.8, 30.9, 29.5.

All the above reactions are given in Scheme 1.

## 2.4. Characterization methods

Infrared spectra were measured in the range 4000–400  $\text{cm}^{-1}$  for the monomer in KBr disks on a JASCO IR-700 Spectrometer. Elemental analysis of the monomer was conducted on a Perkin–Elmer 2400 instrument. Thermogravimetric analysis was measured on a Du Pont 2200 instrument at a heating rate of 10°C  $\text{min}^{-1}$  in nitrogen. The glass transition temperature ( $T_g$ ) was measured with a Du Pont 9000 differential scanning calorimeter at a heating rate of 10°C  $\text{min}^{-1}$ . The fluorescence emission spectra of polymer film were recorded on a SHMASU RF-530 fluorescence-meter. Weight-average ( $\bar{M}_w$ ) and number-average molecular weight ( $\bar{M}_n$ ) were determined by gel permeation chromatography (GPC). Three Waters (Ultrastayragel) columns 300  $\times$  7.7 mm (500,  $10^3$ ,  $10^4$  Å in a series) were used for GPC analysis with THF (1 ml  $\text{min}^{-1}$ ) as the eluent. The eluents were monitored with a UV detector (Gilson model 116) at 254 nm. Polystyrene was used as the standard.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were taken on a JEOL EX-400 operating at 399.65 MHz for proton and 100.40 MHz for carbon. Transmission electron microscopy (TEM) was performed on a JEOL FX-2000II instrument operating at 80 kV.

## 3. Results and discussion

### 3.1. Polymerization and characterization

The polymerization of CbzNB using  $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$  as catalyst in methylene chloride was observed to proceed smoothly at room temperature affording homopolymer in high yield (greater than 98%, Scheme 1 (3)). For comparison,  $^1\text{H}$  NMR spectra of both the monomer and the polymer are shown in Fig. 1(a) and (b), respectively. Integration of the aromatic (7.1–8.0 ppm) and olefin regions (5.0–5.6 ppm) (Fig. 1(b)) of the spectrum gives the expected 4:1 ratio, providing further confirmation of the polymer structure [10]. The resultant polymer is the mixture of *cis*- and *trans*-configuration as well as contains head-to-head, head-to-tail, and tail-to-tail arrangement of the repeated unit.

### 3.2. Hydrogenated poly(CbzNB)

Since thermal instability of the poly(CbzNB) is largely due to the unsaturation of the main chain, poly(CbzNB) was hydrogenated by *p*-toluenesulfonylhydrazide. According to a previous paper [21], diimide ( $\text{NH}=\text{NH}$ ) has been used for the hydrogenation of olefinic compounds and unsaturated polymer. An important feature of diimide hydrogenation is its selectivity. Only non-polar double bonds are active; polar double bonds and aromatic ring systems are inert. The *p*-toluenesulfonylhydrazide was used as a convenient precursor to generate diimide in situ [22]. The  $^1\text{H}$  NMR spectrum of the hydrogenated poly(CbzNB) obtained by *p*-toluenesulfonylhydrazide was measured in deuterated chloroform (Fig. 1(c)). There was no olefinic resonance visible after hydrogenation. That is, before hydrogenation (Fig. 1(b)), there were olefinic resonances between 5.0 and 5.6 ppm; and after hydrogenation (Fig. 1(c)), the resonances completely disappeared. The aromatic resonances of the hydrogenated poly(CbzNB) between 7.1 and 8.0 ppm, (Fig. 1(c)) still exist, suggesting that the carbazole group had remained unchanged.

### 3.3. Thermal properties and solubility

The poly(CbzNB)s with various molecular weights have glass transition temperatures ( $T_g$ ) between 154 and 160°C (Table 1) and no remarkable difference was observed. The 10% decomposition temperature between 403 and 410°C was observed in nitrogen atmosphere. Furthermore, no remarkable difference was observed, indicating that the poly(CbzNB)s exhibited very high thermal stability. The thermal properties of poly(CbzNB), block copolymer and hydrogenated poly(CbzNB) are shown in Table 2. As shown in Fig. 2, saturation of the double bond for poly(CbzNB) led to an increase in decomposition temperature of about 45°C under nitrogen. A decrease in  $T_g$  caused by hydrogenated polymer was about 20°C. Obviously, the rotation around the

Table 1

Polymerization results for CbzNB at various [M]/[I] molar ratios by  $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$  at 25°C ([M] = 0.243 M, polymerization solvent: methylene chloride. Determined by GPC using polystyrene calibration standards)

[M]/[I]	Yield <sup>a</sup> (%)	$\bar{M}_n$ (calculated)	$\bar{M}_n$ (observed)	PDI	$T_g$ <sup>b</sup> (°C)	$T_d^{10\%}$ <sup>c</sup> (°C)
100	97	27 300	26 400	1.29	158	403
300	98	81 900	86 000	1.27	155	410
700	98	191 100	193 000	1.28	154	410
1200	99	327 600	328 700	1.28	160	410

<sup>a</sup> Polymerization time: 1 h.

<sup>b</sup> Analysis by differential scanning calorimetry with a scan rate of 10°C min<sup>-1</sup>.

<sup>c</sup> Analysis by thermal gravimetric analysis with a scan rate of 10°C min<sup>-1</sup>.

hydrogenated carbon–carbon single bond made the mobility of the polymer chain easier[23].

Polymers 3–5 (Scheme 1) were all highly soluble in common organic solvents such as THF, chloroform and methylene chloride, but insoluble in DMSO and DMF. Hydrolyzed block copolymer 6 (Scheme 1) was only soluble in THF but insoluble in methylene chloride, chloroform and DMSO. The GPC trace (Fig. 3(c)) showed a low polymer molecular weight, consistent with loss of the bulky trimethylsilyl group. The molecular weight distribution also appeared to broaden a little, possibly as a result of some sort of aggregation phenomenon cause by hydrogen bonding interaction between free hydroxyl groups of the polymer chain [10].

### 3.4. Block copolymerization

The living nature of the polymerization was demonstrated by adding a small amount of 5-[(trimethylsilyloxy) methylene]-2-norbornene (NBTMS) to the unreacted mixture to form a block copolymer. GPC analysis in Fig. 3(b) shows a clear increase in molecular weight relative to the homopolymer (Fig. 3(a)) with a narrow molecular weight distribution (PDI = 1.25). <sup>1</sup>H NMR analysis of the block copolymer (Fig. 4(a)) showed a relatively sharp, intense peak at 0.1 ppm arising from the nine equivalent protons of the trimethylsilyl group. Furthermore, from the measurement of GPC (Fig. 3, described above), the increase in molecular weight of the block copolymer showed that the

two blocks had approximately equal degrees of polymerization, according to the employed reaction stoichiometry.

The hydrolysis of block copolymer 5 (Scheme 1) was carried out under acidic conditions to remove the trimethylsilyl protecting groups from the polymer and unmask the alcohol functionalities (copolymer 6, Scheme 1). Analysis of the hydrolyzed product 6 by <sup>1</sup>H NMR (Fig. 4(b)) showed that removal of the trimethylsilyl group was nearly quantitative. The GPC trace (Fig. 3(c)) showed a clear decrease in polymers molecular weight consistent with loss of the bulky trimethyl silyl group. As mentioned above, the molecular weight distribution appeared to broaden a little, possibly as a result of some aggregations caused by hydrogen-bonding interaction between free hydroxyl groups of the polymer chain [10].

### 3.5. Living polymerization

To fully investigate the polymerization, the dependence of the number average molecular weight ( $\bar{M}_n$ ) on the [M] : [I] ratio was studied ([M] = monomer concentration, [I] = initiator concentration). The dependence was linear for poly(CbzNB) providing control over the polymer molecular weight, and the polymers produced were of low polydispersity between 1.2 and 1.3 for all ratios (Table 1, Fig. 5). The linear dependence observed was indicative of a living polymerization [24], but further proof was necessary. In addition to the molecular weight study, evidence for the lack of chain transfer and chain termination reaction must be demonstrated to prove that a polymerization is in progress. A sequential monomer addition experiment was run for CbzNB. With complex 1  $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$ , 50 equiv. of CbzNB were polymerized for 1 h under typical conditions. The solution was then divided into three portions. Portion A was removed and its molecular weight was determined by GPC. Portion B was stirred for an additional 5 h. To portion C was added an additional 800 equiv. of CbzNB, and stirred for an additional 1 h before being terminated. Portions B and C were then analyzed by GPC.

As seen in Fig. 6, no significant change was observed from the 1 h reaction (a)  $\bar{M}_n = 13 600$  and PDI = 1.21 and the 6 h reaction (b)  $\bar{M}_n = 13 700$  and PDI = 1.25. If

Table 2

The thermal properties of poly(CbzNB), block copolymer and hydrogenated poly(CbzNB)

Polymer code		$T_g$ <sup>a</sup> (°C)	$T_d^{10\%}$ <sup>b</sup> (°C)
I	Poly(CbzNB) [M]/[I] = 200	160	410
II	Poly(CbzNB) [M]/[I] = 200(hydrogenated)	141	445
III	Poly(CbzNB- <i>b</i> -NBTMS)	157	410
IV	Poly(CbzNB- <i>b</i> -NBOH)	118, 160	410

<sup>a</sup> Analysis by differential scanning calorimetry with a scan rate of 10°C min<sup>-1</sup>.

<sup>b</sup> Analysis by thermal gravimetric analysis with a scan rate of 10°C min<sup>-1</sup> under nitrogen.

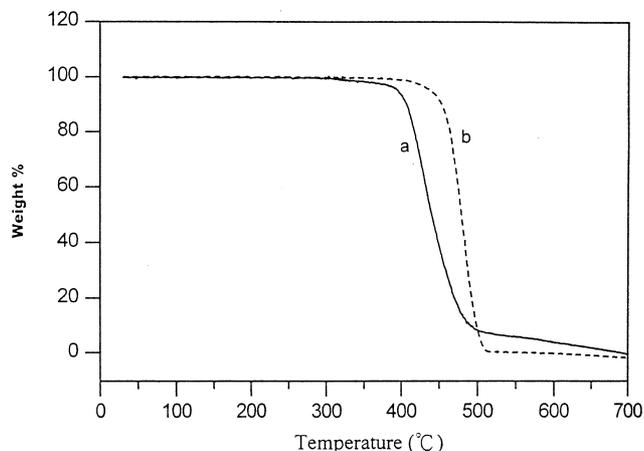


Fig. 2. TGA curves for poly(CbzNB) (a) and hydrogenated poly(CbzNB) (b) measured under nitrogen. Temperature was raised at rate of  $10^{\circ}\text{C min}^{-1}$ .

any significant chain transfer process had been operative during this time, broadening of the PDI would have been observed. Portion C, in which an  $\bar{M}_n$  of additional 750 equiv. of CbzNB were polymerized, resulted in  $\bar{M}_n = 219700$  and  $\text{PDI} = 1.25$ . A clean shift in the GPC peaks was accomplished, which proved that no chain termination processes had occurred. Chain-termination would have resulted in inactive chain ends after polymerization of the first 50 equiv. of CbzNB, which would produce a bimodal GPC trace after additional polymerization. The absence of both chain-transfer and chain-termination reaction was indicative of a living polymerization of the CbzNB [24].

### 3.6. Fluorescence

The fluorescence emission spectra of (a) poly(CbzNB);

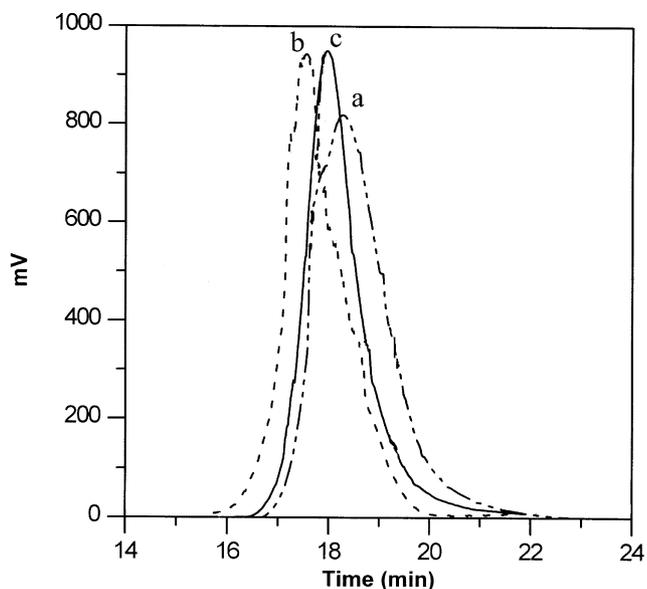


Fig. 3. GPC elution profiles (taken in THF at room temperature at a flow rate of  $1.0 \text{ ml min}^{-1}$ ): (a) homopolymer 3; (b) block copolymer 5; (c) deprotected block copolymer 6.

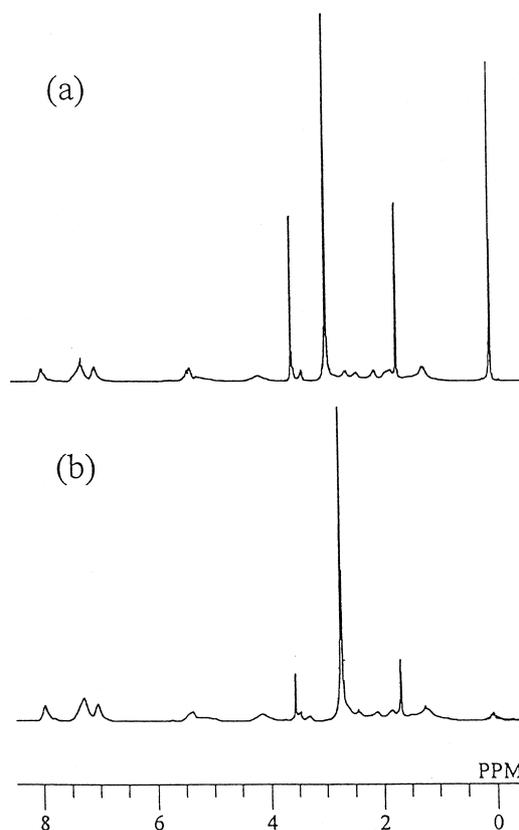


Fig. 4. 400 MHz  $^1\text{H}$  NMR spectra taken in  $\text{THF-d}_8$  at  $25^{\circ}\text{C}$ : (a) TMS-protected block copolymer 5; (b) deprotected block copolymer 6.

(b) hydrogenated poly(CbzNB); and (c) poly(*N*-vinyl carbazole) (PVK) were recorded (Fig. 7). Poly(CbzNB) exhibited a strong carbazole fluorescence, which had monomer emission occurring in the near-UV approximately at 377 nm and extending into the blue-violet region of the

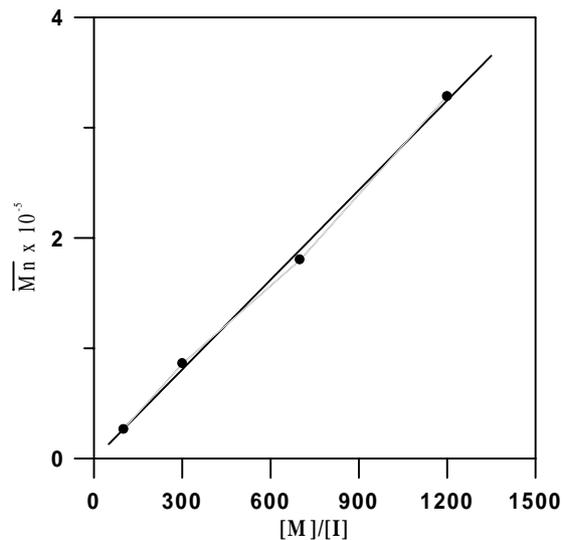


Fig. 5. Molecular weight dependence of the polymerization of CbzNB on  $[\text{M}] : [\text{I}]$ ,  $[\text{M}]$ : concentration of CbzNB;  $[\text{I}]$ : concentration of initiator.

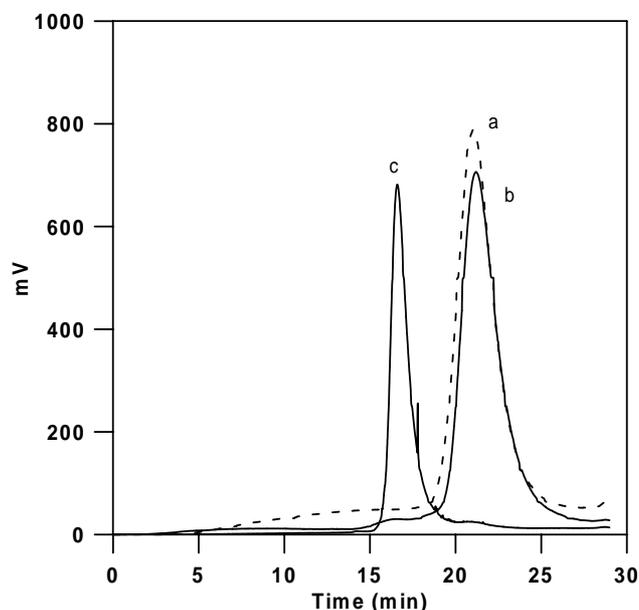


Fig. 6. Sequential monomer addition experiment (a) with 50 equiv. of CbzNB after 1 h; (b) with 50 equiv. of CbzNB after 6 h; and (c) after an additional 750 equiv. of CbzNB was added.

spectrum. A low-level emission observed at higher wavelengths (480 nm) was probably due to excimer formation [10]. Hydrogenated poly(CbzNB) exhibited the same monomer emission in the near-UV approximately at 377 nm; and no low-level emission was observed, indicating that the mobility of the main chain of hydrogenated poly(CbzNB) increased because of the saturation of the double bonds, which decreased the ability of the excimer formation [23]. Neither poly(CbzNB) nor hydrogenated poly(CbzNB) had peaks corresponding to the excimer peak of the PVK.

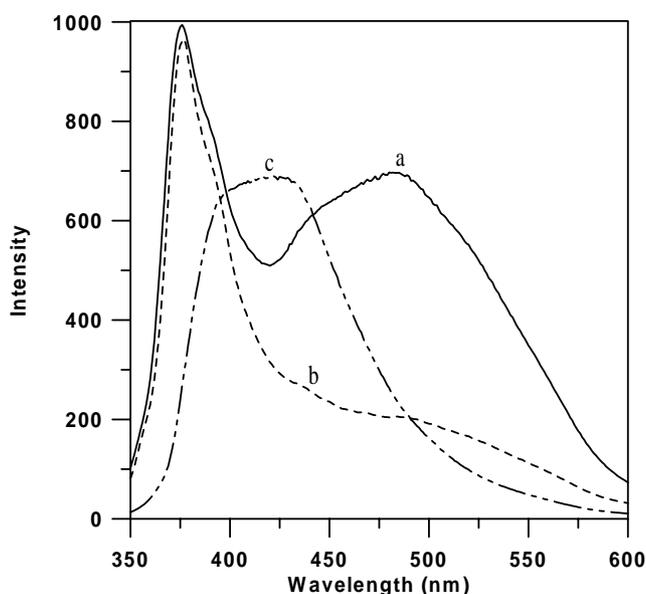


Fig. 7. Fluorescence spectra of (a) poly(CbzNB): (—); (b) hydrogenated poly(CbzNB):(- - -); (c) PVK:(- · - ·).

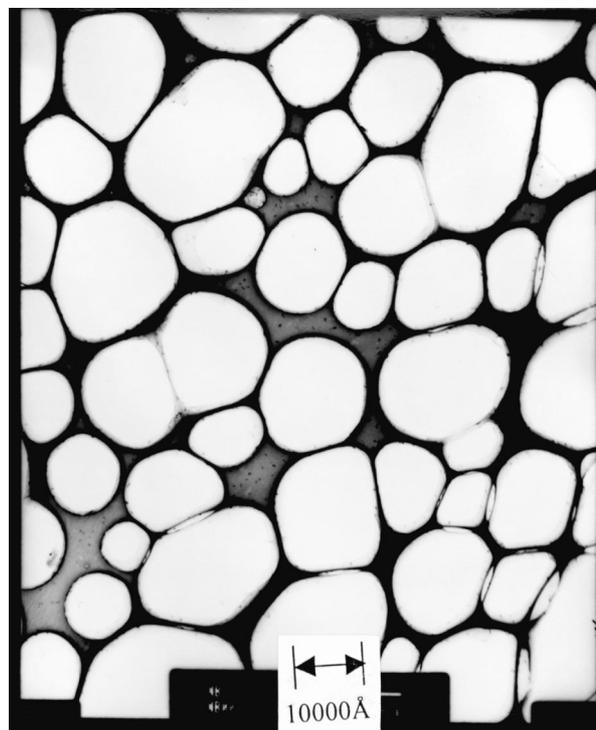


Fig. 8. Transmission electron microscopy micrograph of polymer 6.

### 3.7. Transmission electron microscopy

Microphase separation in block copolymer 6 (Scheme 1) was observed by TEM (Fig. 8) using casting thin film which was stained by exposure to dimethyl cadmium vapor overnight, and pumped down under vacuum. The second block hydroxy group showed a much smaller volume fraction than the carbazole group of the sample. The alcohol domain was formed presumably by direct reaction of dimethyl cadmium with this group to form a bound metal alkoxide and methane [10]. However, strong binding between dimethyl cadmium and carbazole nitrogen did not occur because of the aforementioned low basicity of the carbazole group.

## 4. Conclusion

This study provided interesting results for the living ring-opening metathesis polymerization of a new carbazole-functionalized norbornene derivative (CbzNB). The resulting polymer was of high molecular weight and had a narrow molecular weight distribution. Hydrogenation of poly(CbzNB) increased the thermal stability of the polymer. The linear dependence of the number average molecular weight ( $\bar{M}_n$ ) on the  $[M] : [I]$  ratio and low polydispersity demonstrated a living polymerization of CbzNB. The fluorescence emission spectrum of the poly(CbzNB) exhibited a strong carbazole fluorescence. Microphase separation observed by TEM in the block copolymer 6 (Scheme 1)

displayed a strong binding of cadmium into the alcohol domain.

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