

Synthesis and characterization of new diblock copolymers of 5-(*N*-carbazolyl methyl)bicyclo[2.2.1]hept-2-ene and 1,5-cyclooctadiene using ring opening metathesis polymerization (ROMP)

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Abstract

The novel diblock copolymer of 5-(*N*-carbazolyl methyl)bicyclo[2.2.1]hept-2-ene (CbzNB) with 1,5-cyclooctadiene (COD) has been synthesized by ring opening metathesis polymerization (ROMP) using a well-defined catalyst, $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$. The diblock copolymers were characterized by means of gel permeation chromatography (GPC), ^1H nuclear magnetic resonance (NMR), UV-visible, fluorescence, dynamic light scattering (DLS), differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA). The molecular weight distributions of the diblock copolymers are narrow ($\overline{M}_w/\overline{M}_n = 1.10\text{--}1.47$). Diblock copolymers showed four distinct UV absorptions characteristic of the carbazole group at 255, 295, 319 and 332 nm. Diblock copolymers exhibited a strong carbazole fluorescence, with monomer emission occurring in the near-UV at approximately 377 nm and extending into the blue-violet region (470 nm). In tetrahydrofuran and methylene chloride solution, the emission around 470 nm was not observed. Diblock copolymers showed two T_g values owing to poly(CbzNB) and polybutadiene segments. However, after hydrogenation, they showed only one T_g for poly(CbzNB) segment and one T_m for polyethylene segment. The diblock copolymer [poly(CbzNB-*b*-PB)-1] with longer CbzNB chain exhibited better thermal stability than copolymer with shorter CbzNB chain [poly(CbzNB-*b*-PB)-2]. Two kinds of hydrogenated diblock copolymers, hydrogenated poly(CbzNB-*b*-PB)-1 and hydrogenated poly(CbzNB-*b*-PB)-2, have poorer solubility, but better thermal stability than unhydrogenated diblock copolymers, owing to the polyethylene segments. Furthermore, the larger hydrodynamic diameter of 324.2 nm was obtained after hydrogenation, indicating that the mobility of the main chain was increased. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ring opening metathesis polymerization (ROMP); 5-(*N*-carbazolyl methyl)bicyclo[2.2.1]hept-2-ene; 1,5-Cyclooctadiene; Diblock

1. Introduction

Controlled/“living” polymerization methods offer an efficient way to prepare well-defined

polymers in systems where the contributions of side reactions are small. In these systems, the polymerization proceeds until all of the monomers have been consumed, and further addition of monomer results in continued polymerization. Living or controlled/“living” polymerization can proceed by anionic [1], cationic [2], group transfer [3], metathesis [4,5],

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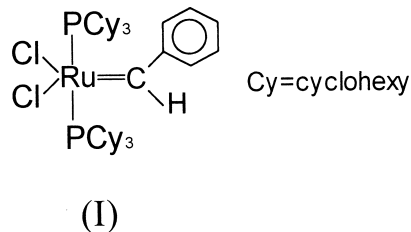
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Ziegler–Natta [6], or radical [7,8] mechanisms. These polymerization techniques give several avenues to synthesize the block copolymers.

Block copolymers have attracted attention for many years since they have been recognized as materials that combine the properties of two completely different polymers. Polymers that contain pendant carbazole groups exhibit many interesting behaviors such as photoconductivity and electrochemical properties [9–12]. Carbazolyl-substituted polymers are well known as precursors for electrophotographical materials with valuable optical, photoconductive, and other useful applications such as organic light-emitting diodes [13]. Since the first application of poly(*N*-vinylcarbazole) in xerography [14], great interest has focused on photoconductivity and electrochemical property of carbazole-containing polymers [15–17]. Carbazole-functionalized bicyclo[2.2.1]hept-2-ene derivatives have been polymerized recently using classical, non-living olefin metathesis catalysts such as RuCl_3 , and $\text{RuCl}_2(\text{PPh}_3)_3$ [18,19]. 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.

In previous work, 5-(*N*-carbazolyl methyl)bicyclo[2.2.1]hept-2-ene (CbzNB) was successfully synthesized and its homopolymer also was prepared via living ring opening metathesis polymerization (ROMP) [9]. The poly{5-(*N*-carbazolyl methyl)bicyclo[2.2.1]hept-2-ene} proceeds in a living fashion, and the molecular weight can be regulated easily by changing the ratio of monomer to catalyst [9]. Furthermore, hydrogenation of the poly{5-(*N*-carbazolyl methyl)bicyclo[2.2.1]hept-2-ene} had been carried out and excellent thermal stability was obtained [9]. In this study, new diblock copolymers of a carbazole-functionalized bicyclo[2.2.1]hept-2-ene derivative poly(Cbz-NB-*b*-PB)-1 and poly(CbzNB-*b*-PB)-2 having different carbazole

contents and corresponding hydrogenated polymers by using the complex (I)



were synthesized. The diblock copolymers have various lengths of CbzNB and 1,5-cyclooctadiene (COD) segments. The characterization of diblock copolymers, such as UV–visible absorption, fluorescence emission spectra, solubility and thermal properties was also investigated.

2. Experimental

2.1. Materials

Bis(tricyclohexylphosphine) - benzylideneruthenium dichloride $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$ was purchased from Strem, USA. Dicyclopentadiene and allyl chloride were purchased from Merck, Germany. *p*-Toluenesulfonylhydrazide, 2,6-di-*tert*-butyl-4-methylphenol (BHT) and COD were purchased from Acros, Belgium, and used without further purification. Solvent such as xylene was 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 5-(chloromethyl)bicyclo[2.2.1]hept-2-ene (bp = 54–56°C/11 mm Hg) was accomplished via the Diels–Alder reaction of freshly cracked dicyclopentadiene and allyl chloride [9].

2.2. Monomer synthesis

2.2.1. CbzNB

Monomer, CbzNB, was synthesized from 5-(chloromethyl)bicyclo[2.2.1]hept-2-ene and potassium salt of carbazole as reported previously [9], mp = 74–76°C[endo/exo = 3:2, ^1H nuclear magnetic resonance (NMR) (CDCl_3), 6.15 (m, = CH, endo), 6.06 (m, = CH, endo), 5.95 (m, = CH, exo), 7.75, 7.60 (m, 8H, aromatic)].

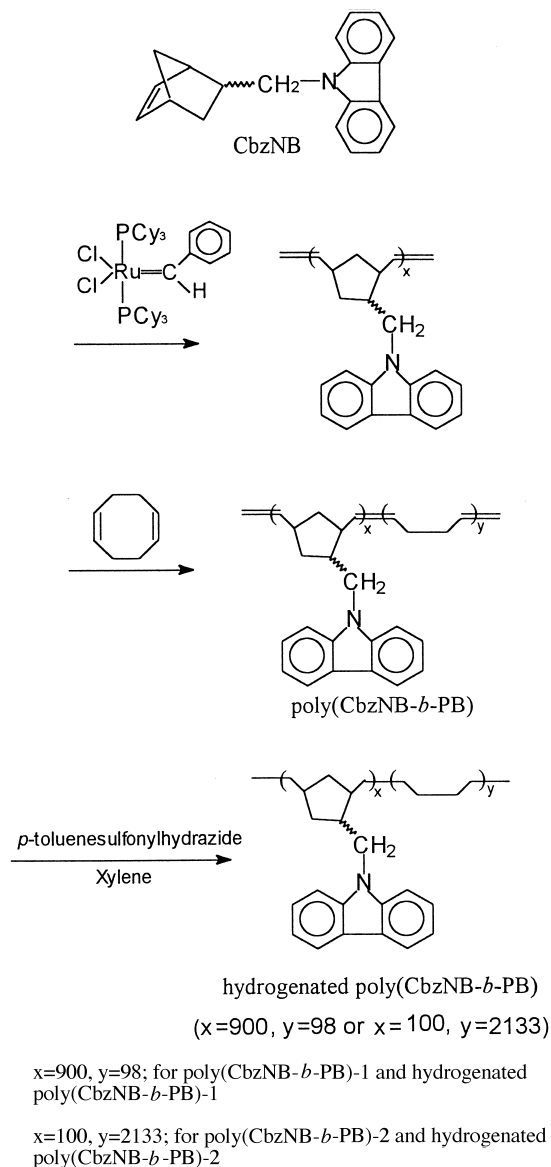
2.3. Polymerization

2.3.1. Preparation of block copolymer, [poly(CbzNB-*b*-PB)-1]

A solution of catalyst was prepared by dissolving $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$ (1.65 mg, 2×10^{-6} mol) in 1 ml of anhydrous methylene chloride under argon-filled drybox. The monomer, CbzNB (0.5 g, 1.83×10^{-3} mol), was dissolved in 5 ml of methylene chloride and then degassed via a freeze–pump–thaw cycle. After complete degassing, the catalyst solution was injected into the monomer solution by syringe. The pink solution was vigorously stirred at room temperature for 30 min. COD (0.2 g, 1.85 mmol) was injected to the still-living reaction mixture and the solution was stirred for another 12 h at room temperature. The color of the solution changed from pink to yellow after COD was added. The reaction was terminated by the addition of a small amount of ethyl vinyl ether (0.5 ml). After termination, the solution was stirred for an additional 5 min, and the polymer, [poly(CbzNB-*b*-PB)-1], was precipitated in excess of methanol and dried overnight in a vacuum system at room temperature to give a flaky white solid in essentially quantitative yield [20,21]. Yield = 80%. Almost all of the CbzNB monomer could be consumed, but only 30% of COD was polymerized after 12 h. Unreacted monomer and oligomers were removed by reprecipitated from methylene chloride to excess of methanol three times.

The synthetic method of poly(CbzNB-*b*-PB)-2 having a shorter segment of carbazole group (Scheme 1) was the same as poly(CbzNB-*b*-PB)-1 except for the different amount of CbzNB (0.056 g, 0.21 mmol) and COD (5.5 g, 0.051 mol). Yield = 30%.

The diblock copolymer, [poly(CbzNB-*b*-PB)-1], compositions have been calculated by ^1H NMR spectra. The mole fractions of the copoly-



Scheme 1.

mer were estimated from the relative peak area of unsaturation double bond proton resonance for poly(CbzNB) and polybutadiene, and the peak area of carbazole proton resonance. Carbazole proton resonance generally appears between 6.9 and 8.3 ppm [9]. The unsaturation double bond proton resonance in the polymer main chain for poly(CbzNB) and polybutadiene appears between 4.7 and 5.8 ppm.

2.3.2. Hydrogenation of block copolymer, [poly(CbzNB-*b*-PB)-1]

In a typical experiment, poly(CbzNB-*b*-PB)-1 (0.5 g) was dissolved in 50 ml of xylene in an ampoule. To the above solution were added 2.75 g of *p*-toluenesulfonylhydrazide as a hydrogenation agent and a trace of BHT. The ampoule containing the polymer, solvent and hydrogenation agent was then degassed thrice via a freeze–pump–thaw cycle and sealed. Then, it was gradually 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 with methanol. It was dissolved in methylene chloride and reprecipitated with methanol to further purify the white polymer. The hydrogenated polymer, hydrogenated poly(CbzNB-*b*-PB)-1, was dried in vacuum overnight at room temperature. Yield = 94%. The synthetic method of hydrogenated poly(CbzNB-*b*-PB)-2 having a shorter segment of carbazole group (Scheme 1) was the same as hydrogenated poly(CbzNB-*b*-PB)-1. All of polymerizations are shown in Scheme 1.

2.4. Characterization methods

Thermogravimetric analysis (TGA) was measured on Du Pont 2200 instrument at a heating rate of 20°C min⁻¹ in nitrogen. The glass transition temperature (T_g) was measured with a Du Pont 9000 differential scanning calorimeter (DSC) at a heating rate of 20°C min⁻¹. Weight average (\overline{M}_w) and number average (\overline{M}_n) molec-

ular weight were determined by gel permeation chromatography (GPC). Polystyrene was used as the standard. Four Waters (Ultrastayragel) columns 300 × 7.7 mm² (500, 10³, 10⁴, 10⁵ Å in a series) were used for GPC analysis with tetrahydrofuran (THF) (1 ml min⁻¹) as the eluent. The eluents were monitored with a UV detector (Gilson model 116) at 254 nm. The fluorescence emission spectra of the polymer film and solution were recorded by a SHIMADZU RF-530 fluorescence meter. Dynamic light scattering (DLS) measurements were made on 0.01 g dl⁻¹ copolymer solutions (in methylene chloride) at a fixed scattering angle of 90°, using OTSUKA DLS7000 spectrometer. ¹H NMR spectrum was taken on a JEOL EX-400 operating at 399.65 MHz, and tetramethylsilane (TMS) was used as the standard.

3. Results and discussion

3.1. Characterization of diblock copolymers

Diblock copolymers of CbzNB with COD have been synthesized by ROMP using well defined {Cl₂Ru(CHPh)[P(C₆H₁₁)₃]₂} as catalyst (Scheme 1). The ¹H NMR spectra for both block copolymers before and after hydrogenation are shown in Fig. 1. Integration of the aromatic and olefin regions of the spectrum gives the expected ratio, providing further confirmation of the polymer structure [9]. Before hydrogenation, the broad resonances at 4.7–5.8 ppm for the olefinic protons, and the *cis* content could not be quantitatively determined by ¹H NMR due to peak overlap in this region [22]. After hydrogenation, the resonances between 4.7 and 5.8 ppm completely disappeared. The aromatic resonances of the hydrogenated copolymers between 6.9 and 8.3 ppm (Fig. 1) still appeared, which suggests that the carbazole group remained unchanged. In fact, the peak around 1 ppm due to polynorbornene backbone ring structure (–CH₂–) did not disappear (Fig. 1a) [23,24], but overlapped with the broad reso-

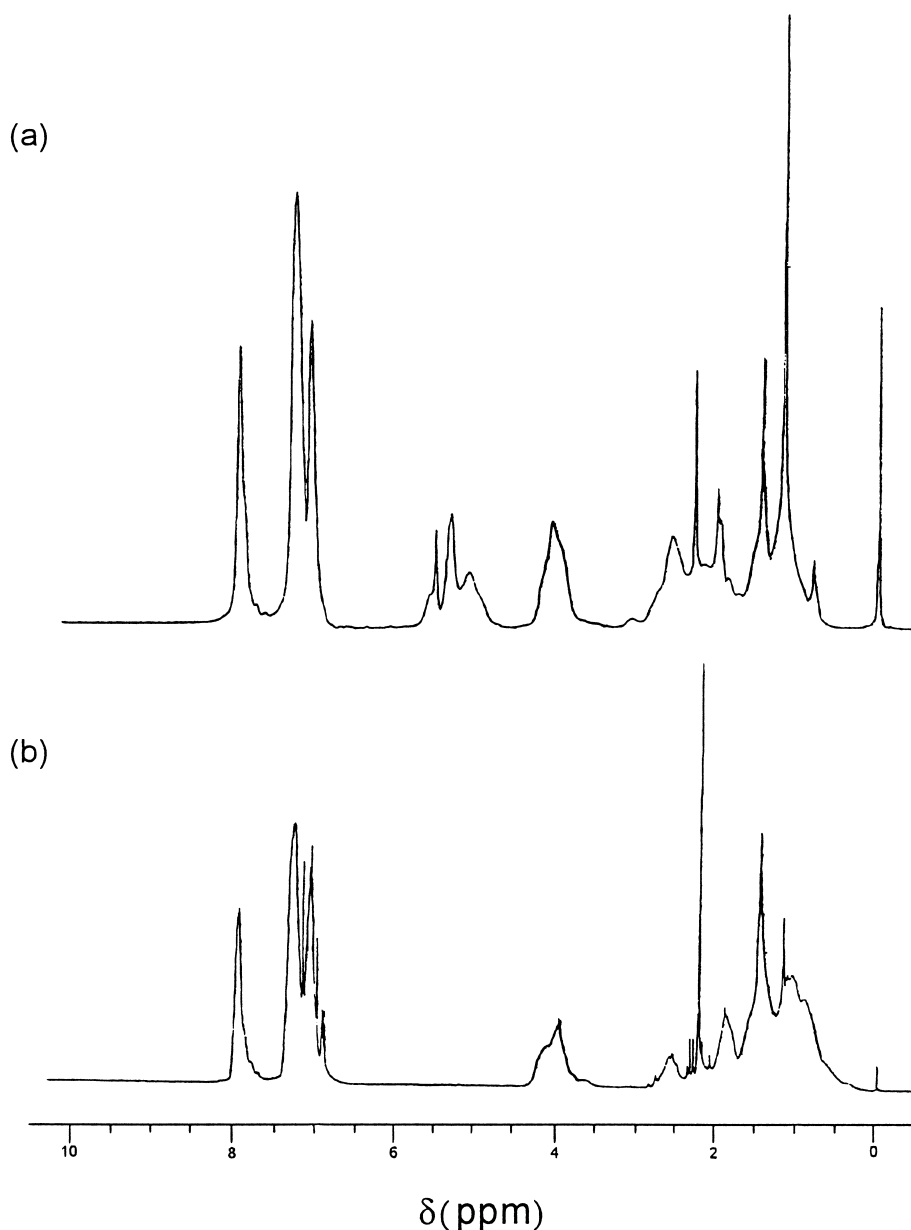


Fig. 1. The ^1H NMR spectra of (a) poly(CbzNB-*b*-PB)-1; (b) hydrogenated poly(CbzNB-*b*-PB)-1 (solvent: CDCl_3).

nance around 0.5–1.8 ppm due to the formed methylene group of polyethylene segment (Fig. 1b).

CbzNB can be polymerized in a living manner employing $\{\text{Cl}_2\text{Ru}(\text{CHPh})[\text{P}(\text{C}_6\text{H}_{11})_3]_2\}$ as the catalyst, and the conversion of CbzNB homopolymer was near 99% when the ratio of $[\text{monomer}]/[\text{initiator}]$ was 900 [9]. The degree

of polymerization for CbzNB segments (DP_{CbzNB}) was calculated according to Eq. 1:

$$\text{DP}_{\text{CbzNB}} = \left\{ \frac{[\text{monomer}]}{[\text{initiator}]} \right\} \times \text{conversion}, \quad (1)$$

where $[\text{monomer}]$ and $[\text{initiator}]$ represent the initial concentrations of monomer (CbzNB) and catalyst [complex (I)], respectively. However,

Table 1

A summary of the molecular weight, polydispersities and copolymers composition

Polymer	CbzNB content ^a (mol%)	CbzNB content ^b (mol%)	\overline{M}_n (g mol ⁻¹)	$\overline{M}_w/\overline{M}_n$ ^c
Poly(CbzNB- <i>b</i> -PB)-1	94.5	90.2	251,000	1.42
Poly(CbzNB- <i>b</i> -PB)-2	5.8	4.5	142,500	1.10
Hydrogenated poly(CbzNB- <i>b</i> -PB)-1	91.8	84.7	255,100	1.47
Hydrogenated poly(CbzNB- <i>b</i> -PB)-2	– ^d	– ^d	– ^d	– ^d

^aAs determined by ¹H NMR spectroscopy (the calculation method was described in Section 2).^bAs determined by GPC elution profiles: CbzNB content for poly(CbzNB-*b*-PB)-1 and poly(CbzNB-*b*-PB)-2 in mol% = $DP_{\text{CbzNB}}/(DP_{\text{CbzNB}} + DP_{\text{butadiene}})$ or CbzNB content for hydrogenated poly(CbzNB-*b*-PB)-1 in mol% = $DP_{\text{CbzNB}}/(DP_{\text{CbzNB}} + DP_{\text{ethylene}})$.^cAs determined by GPC in THF using polystyrene as a calibration standard.^dHydrogenated poly(CbzNB-*b*-PB)-2 could not be soluble in CDCl₃ and THF.

COD exhibits a rather low reactivity for ROMP [25]. Thus, the apparent degree of polymerization for butadiene segments ($DP_{\text{butadiene}}$) would be determined by various measurements. In this study, the apparent degree of polymerization for butadiene segments ($DP_{\text{butadiene}}$) was calculated with the following schematic Eq. 2:

$$DP_{\text{butadiene}} = \frac{(\overline{M}_{\text{GPC}} - \overline{M}_{\text{CbzNB(th)}})}{M_{\text{butadiene}}} \quad (2)$$

where $\overline{M}_{\text{GPC}}$ is the molecular weight of copolymer determined from GPC, $\overline{M}_{\text{CbzNB(th)}}$ is the theoretical molecular weight calculated in accordance with $[\text{monomer}]/[\text{initiator}]$ ratio, and $M_{\text{butadiene}}$ is the molecular weight of butadiene. For poly(CbzNB-*b*-PB)-1, $DP_{\text{butadiene}}$ of 98 was obtained. The CbzNB content, molecular weight and polydispersities of these copolymers are shown in Table 1.

From Table 1, narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n = 1.10\text{--}1.47$) were observed. The CbzNB content in copolymers was determined by ¹H NMR spectroscopy, and agreement between the ¹H NMR measurement and the calculated values by GPC was obtained. GPC measurements showed that the molecular weight distribution of poly(CbzNB-*b*-PB)-1 and poly(CbzNB-*b*-PB)-2 are unimodal and narrow (Fig. 2a and b). From Fig. 2, as the $[\text{monomer}]/[\text{initiator}]$ ratio decreased from 900 to 100 for CbzNB, the corresponding polymers, poly(CbzNB-*b*-PB)-1 and poly(CbzNB-*b*-PB)-2, were obtained, respectively. Also, the clear shift

of molecular weights without any shoulder indicates clean formation of block copolymers.

3.2. UV, fluorescence and hydrodynamic diameters of the copolymers

Poly(CbzNB-*b*-PB)-1 showed four distinct UV absorptions characteristic of the carbazole group at 255, 295, 319 and 332 nm in methylene chloride. Poly(CbzNB-*b*-PB)-1, poly(CbzNB-*b*-PB)-2, and hydrogenated poly(CbzNB-*b*-

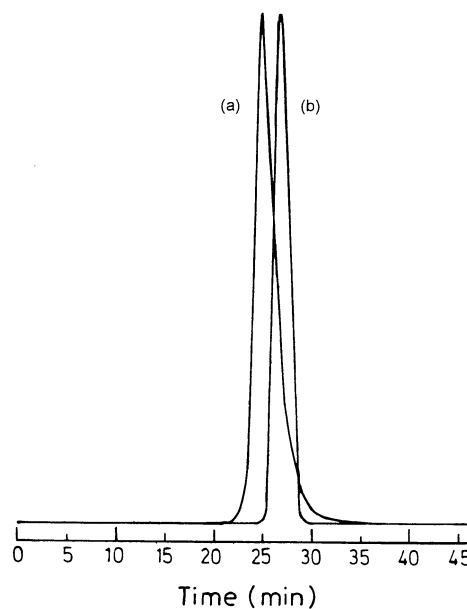


Fig. 2. The GPC elution profiles (taken in THF at room temperature at a flow rate of 1.0 ml min⁻¹): (a) poly(CbzNB-*b*-PB)-1, $[\text{monomer}]/[\text{initiator}] = 900$ for CbzNB; (b) poly(CbzNB-*b*-PB)-2, $[\text{monomer}]/[\text{initiator}] = 100$ for CbzNB.

Table 2
Solubility^a of diblock copolymers in various solvents^b

Polymer	THF	DMAc	Pyridine	DMSO	1,2-Dichloro benzene	Xylene	Toluene	CH ₂ Cl ₂	CHCl ₃	DMF
Poly(CbzNB- <i>b</i> -PB)-1	++	+	++	–	++	+	+	++	++	+–
Poly(CbzNB- <i>b</i> -PB)-2	++	–	++	–	++	++	++	++	++	–
Hydrogenated poly-(CbzNB- <i>b</i> -PB)-1	++	+–	++	–	++	++	++	++	++	–
Hydrogenated poly-(CbzNB- <i>b</i> -PB)-2	–	–	–	–	–	–	–	–	–	–

^aSolubility: ++, soluble at room temperature; +, soluble at a heating temperature of 60°C; +–, partial soluble at 60°C; –, insoluble.

^bAbbreviations: THF, tetrahydrofuran; DMAc, *N,N*-dimethylacetamide; DMSO, dimethylsulfoxide; DMF, *N,N*-dimethylformamide.

PB)-1 could be poured into a 7-cm diameter glass culture dish from tetrahydrofuran and methylene chloride solution to yield optically clear films. The fluorescence spectra exhibited a strong carbazole fluorescence, with monomer emission occurring in the near-UV at approximately 377 nm and extending into the blue-violet region (near 470 nm) [9,26]. In tetrahydrofuran and methylene chloride solution, the emission around 470 nm was not observed. No carbazole fluorescence could be observed for hydrogenated poly(CbzNB-*b*-PB)-2 because of poor solubility in any organic solvent. Hydrodynamic diameters of poly(CbzNB-*b*-PB)-1 (179.2 nm) and hydrogenated poly(CbzNB-*b*-PB)-1 (324.2 nm) were also measured by DLS. The larger hydrodynamic diameter for hydrogenated poly(CbzNB-*b*-PB)-1 was obtained. This result indicates that the mobility of the main chain is easier because of the saturation of the double bonds [9,20].

3.3. Solubility characteristics

The solubility characteristics of the diblock copolymers are shown in Table 2. It was found that the diblock copolymers before hydrogenation [poly(CbzNB-*b*-PB)-1 and poly(CbzNB-*b*-PB)-2] have much better solubility than after hydrogenation [hydrogenated poly(CbzNB-*b*-PB)-1 and hydrogenated poly(CbzNB-*b*-PB)-2]. The solubility of diblock copolymers with longer CbzNB segment [poly(CbzNB-*b*-PB)-1] and shorter CbzNB segment [poly(CbzNB-*b*-PB)-2]

exhibited no remarkable difference. After hydrogenation, the diblock copolymer with longer polyethylene segment [hydrogenated poly(CbzNB-*b*-PB)-2] was insoluble in common organic solvents owing to the polyethylene segment. However, increasing the length of CbzNB segment and lowering the length of polyethylene segment, the solubility has been improved (i.e. for hydrogenated poly(CbzNB-*b*-PB)-1).

3.4. Thermal stability

The glass transition temperature (T_g) values and the melting temperature (T_m) of the diblock copolymers, determined by DSC, are summarized in Table 3. Two T_g values were observed for diblock copolymers before hydrogenation corresponding to the CbzNB (higher T_g value) and butadiene (lower T_g value) segments, which

Table 3
Thermal properties of the diblock copolymers

Polymer	$T_d^{10\%a}$ (°C)	T_g^b (°C)	T_m^b (°C)
Poly(CbzNB- <i>b</i> -PB)-1	400	–85.6, 152.5	– ^c
Poly(CbzNB- <i>b</i> -PB)-2	392	–97.7, 142.0	– ^c
Hydrogenated poly-(CbzNB- <i>b</i> -PB)-1	437	147.8	116.6
Hydrogenated poly-(CbzNB- <i>b</i> -PB)-2	420	146.2	117.2

^aTemperatures at 10% mass loss ($T_d^{10\%}$) were determined by TGA in nitrogen at a heating rate of 20°C min^{–1}.

^bDSC measurements were conducted at a heating rate of 20°C min^{–1}.

^c T_m could not be detected by DSC.

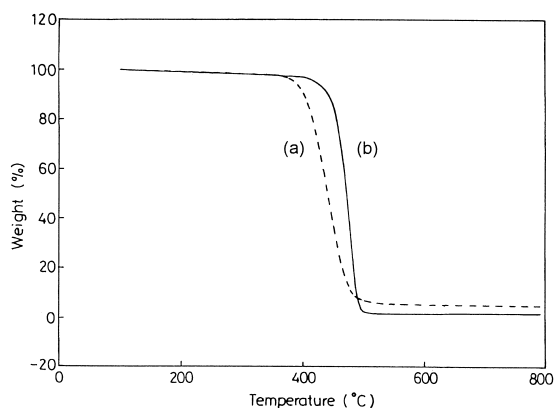


Fig. 3. The TGA curves for (a) poly(CbzNB-*b*-PB)-1 (---), and (b) hydrogenated poly(CbzNB-*b*-PB)-1 (—). Temperature was raised at a rate of 20°C min⁻¹.

indicates that the segments undergo phase segregation. The higher T_g of poly(CbzNB-*b*-PB)-1 was observed than that of poly(CbzNB-*b*-PB)-2, owing to the larger molecular weight of poly(CbzNB-*b*-PB)-1. After hydrogenation, one T_g resulted from hydrogenated polyCbzNB segments, and one T_m from polyethylene segments was observed.

The thermal stability of the diblock copolymers was evaluated by TGA in nitrogen atmosphere at a heating rate 20°C min⁻¹. Fig. 3 shows the TGA curve for poly(CbzNB-*b*-PB)-1 and hydrogenated poly(CbzNB-*b*-PB)-1. From Fig. 3, the diblock copolymer, [poly(CbzNB-*b*-PB)-1], exhibited better thermal stability after hydrogenation. Saturation of the double bond leads to the increase of decomposition temperature under nitrogen 28–37°C [9]. As shown in Table 3, the diblock copolymer with longer CbzNB segment [poly(CbzNB-*b*-PB)-1] exhibited better thermal stability than shorter CbzNB segment [poly(CbzNB-*b*-PB)-2]. Increasing the CbzNB moiety in diblock copolymer, the thermal stability could be improved due to the higher molecular weight and characteristics of carbazole group in diblock copolymer. In general, the incorporation of the carbazole group in the polymer backbone led to an enhanced thermal stability of the polymer [9,26].

4. Conclusions

Two kinds of diblock copolymers having different molecular weights of CbzNB with COD have been successfully synthesized by ROMP using well defined $\{Cl_2Ru(CHPh)[P(C_6H_{11})_3]_2\}$ as catalyst. Agreement for carbazole moiety content in copolymers was obtained by the measurements of ¹H NMR and GPC results. The molecular weight distributions of various diblock copolymers are narrow ($\overline{M_w}/\overline{M_n} = 1.10 - 1.47$). The UV-visible absorption spectra and fluorescence emission spectra showed the characteristics of carbazole group in diblock copolymer. The larger hydrodynamic diameter was observed for hydrogenated poly(CbzNB-*b*-PB)-1 (324.2 nm) than for poly(CbzNB-*b*-PB)-1 (179.2 nm). By increasing the length of the CbzNB segment and lowering the length of the ethylene segment, the solubility was improved. Two T_g values were observed for diblock copolymers before hydrogenation. However, one T_g value and one T_m value were observed for diblock copolymers after hydrogenation due to the CbzNB segments and ethylene segments, respectively. The diblock copolymer with longer CbzNB segment having higher molecular weight [poly(CbzNB-*b*-PB)-1] exhibited better thermal stability than copolymer with shorter CbzNB segment having lower molecular weight [poly(CbzNB-*b*-PB)-2].

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