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Synthesis and characterization of novel diblock copolymers of 5-(*N*-carbazoyl methyl)bicyclo[2.2.1]hept-2-ene and 5-(phthalimide methyl)bicyclo[2.2.1]hept-2-ene via living ring-opening metathesis polymerization

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Abstract

Ring-opening metathesis polymerization (ROMP) has been performed with $\{RuCl_2(CHPh)[P(C_6H_{11})_3]_2\}$ catalyst to make low polydispersity block copolymers of 5-(*N*-carbazoyl methyl)bicyclo[2.2.1]hept-2-ene (CbzNB) and 5-(phthalimide methyl)bicyclo[2.2.1]hept-2-ene (NBMPI). Three diblock copolymers with the CbzNB and NBMPI were made, varying both molecular weight and percent of each block. The hydrogenated diblock copolymers were successfully obtained by using *p*-toluenesulfonylhydrazide as a reducing agent. The novel diblock copolymers were characterized by means of gel permeation chromatography (GPC) ^{1}H NMR, fluorescence, differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA). The molecular weight distributions of the diblock copolymers are narrow ($\overline{M}_w/\overline{M}_n \sim 1.5$). Unhydrogenated diblock copolymers exhibited a strong carbazole fluorescence, with monomer emission occurring in the near-UV at approximately 380 nm and extending into the blue–violet region. Similar results were also observed on hydrogenated diblock copolymers. All diblock copolymers exhibited good solubility in a variety of solvents such as methylene chloride, chloroform, tetrahydrofuran and 1,2-dichlorobenzene; however, there was no remarkable difference between unhydrogenated and hydrogenated diblock copolymers. Two T_g values were observed for the CbzNB segment and the NBMPI segment before and after hydrogenation. Unhydrogenated diblock copolymers exhibited good thermo-oxidative stability, losing 10% mass in the range 369–389°C in air and 400–416°C in nitrogen. However, hydrogenated diblock copolymers showed better thermal stability than unhydrogenated diblock copolymers, and 10% mass loss temperatures were recorded in the range 375–396°C in air and 415–428°C in nitrogen. © 2001 Published by Elsevier Science Ltd.

Keywords: Ring-opening metathesis polymerization; Diblock copolymers; Carbazole

1. Introduction

Ring-opening metathesis polymerization (ROMP) of strained cyclic olefins is an extremely useful technique for the synthesis of new materials [1–4], especially since recent developments of living ROMP methods have allowed the preparation of several novel block copolymers [5]. Synthesis of copolymers and block copolymers with narrow molecular weight distribution and well-defined structure is a subject of both fundamental and practical importance.

Carbazoyl-substituted polymers are well-known as precursors for electrophotographical materials with valuable optical, photoconductive, and other useful applications such as organic light emitting diodes [6]. Since the first application of poly(*N*-vinylcarbazole) in xerography [7], great interest has focused on photoconductivity and electrochemical property of carbazole-contaning polymers [8–10]. Carbazole-functionalized bicyclo[2.2.1]hept-2-ene derivatives have recently been polymerized using classical, non-living olefin metathesis catalysts such as $RuCl_3$, and $RuCl_2(PPh_3)_3$ [11,12]. The resulting homopolymer was reported to exhibit interesting properties, but control over molecular weight and molecular weight distribution was poor, and block copolymers could not be obtained.

Previously, 5-(phthalimidemethyl)bicyclo[2.2.1]hept-2-ene (NBMPI) was successfully synthesized and its homopolymers also was prepared via living ROMP [13,14]. The poly{5-(phthalimide methyl) bicyclo[2.2.1]hept-2-ene} proceeded in a living fashion, and because of the living nature of the polymerization the molecular weight can be regulated

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easily by changing the ratio of monomer to catalyst [13,14]. The incorporation of the phthalimide group remarkably enhanced the thermal stability of the polymer since the phthalimide group is a thermally stable group. The polymer-bearing phthalimide group as a pendent group would exhibit relatively high thermal stability and good solubility [13,14]. Also, 5-(*N*-carbazoyl methyl)bicyclo[2.2.1]hept-2-ene (CbzNB) and poly{5-(*N*-carbazoyl methyl) bicyclo[2.2.1]hept-2-ene} were prepared [15]. The incorporation of the carbazoyl group could further enhance the thermal stability of the polymer and provide electrophotographical properties of the polymers.

In this study, novel diblock copolymers of 5-(*N*-carbazoyl methyl)bicyclo[2.2.1]hept-2-ene (CbzNB) and 5-(phthalimide methyl) bicyclo[2.2.1]hept-2-ene (NBMPI) were successfully synthesized using $\{RuCl_2(CHPh)[P(C_6H_{11})_3]_2\}$ as a catalyst. These diblock copolymers with different CbzNB and NBMPI moieties and their corresponding hydrogenated polymers were obtained by using *p*-toluenesulfonylhydrazide as a reducing agent. The characterization of unhydrogenated and hydrogenated diblock copolymers, such as ^{1}H NMR, fluorescence emission spectra, solubility and thermal properties was also investigated.

2. Experimental section

2.1. Materials

Bis(tricyclohexylphosphine)-benzylideneruthenium dichloride $\{RuCl_2(CHPh)[P(C_6H_{11})_3]_2\}$ was purchased from Strem, USA. Dicyclopentadiene was purchased from Merck, Germany. Phthalic anhydride, carbazole, *p*-toluenesulfonylhydrazide, 2,6-di-*tert*-butyl-4-methylphenol (BHT), allyl chloride and allyl amine were purchased from Acros, Belgium, and was used without further purification. Solvents such as xylene were purified by normal procedures and handled in a moisture-free atmosphere. The polymerization solvent, methylene chloride, was dried over calcium hydride, and distilled before use. The synthesis of 5-(chloro methyl)-bicyclo[2.2.1]hept-2-ene (bp = 54–56°C/11 mmHg) and 5-(amine methyl)bicyclo[2.2.1]hept-2-ene (bp = 60–61°C/11 mmHg) were accomplished via the Diels–Alder reaction of freshly cracked dicyclopentadiene and the corresponding allyl chloride and allyl amine, respectively [13–16].

2.2. Monomer synthesis

2.2.1. 5-(N-carbazoyl methyl)bicyclo[2.2.1]hept-2-ene (CbzNB) [13]

The monomer, 5-(*N*-carbazoyl methyl)bicyclo[2.2.1]-hept-2-ene (CbzNB), was synthesized from 5-(chloro methyl)bicyclo[2.2.1]hept-2-ene and potassium salt of carbazole as reported previously [13], mp = 74–76°C. ^{13}C NMR (100 MHz, $CDCl_3$): 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.

2.2.2. 5-(Phthalimide methyl)bicyclo[2.2.1]hept-2-ene (NBMPI) [14]

The monomer, 5-(phthalimide methyl)bicyclo[2.2.1]-hept-2-ene (NBMPI), was prepared by azotropic removal of water from an equimolar solution of 5-(amine methyl)bicyclo[2.2.1]hept-2-ene and phthalic anhydride in xylene. After removing the solvent, the residue was recrytallized from n-hexane, mp = 99–100°C. ^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm = 168.1, 137.3, 136.6, 135.8, 133.5, 132.4, 131.8, 122.8, 49.3, 44.9, 44.3, 44.2, 43.0, 42.4, 41.8, 41.7, 38.1, 38.0, 30.6.

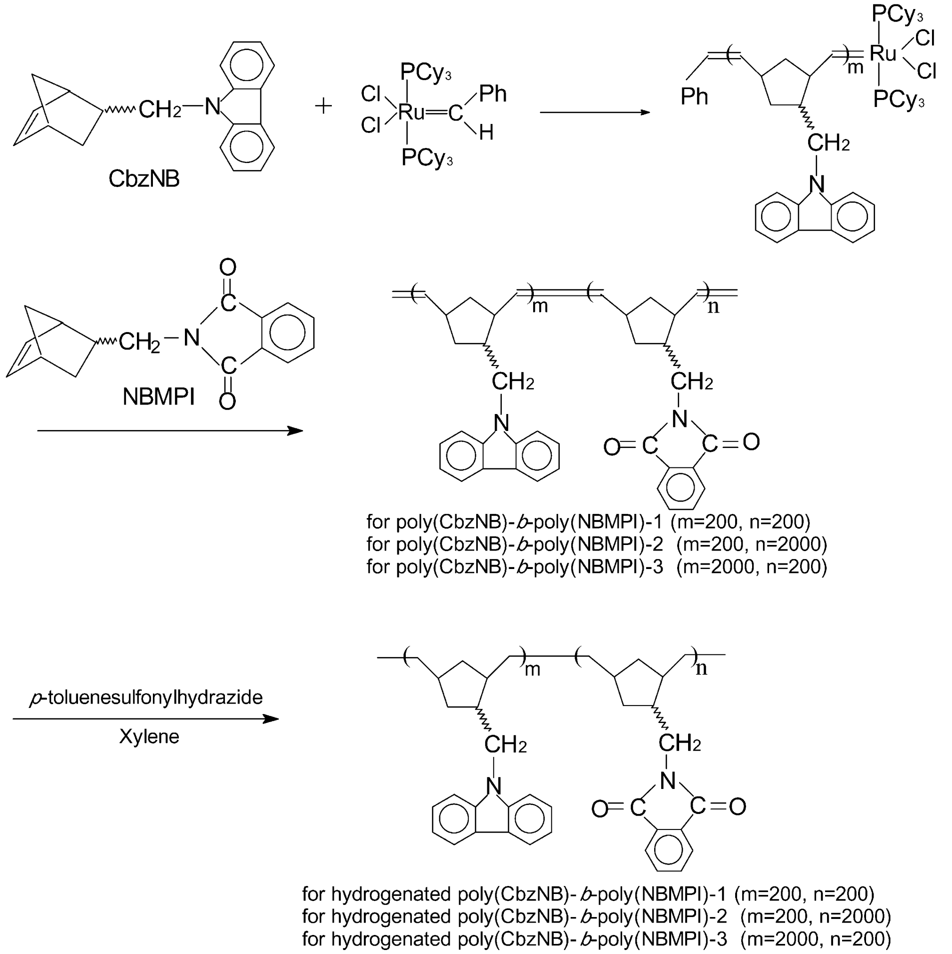
2.3. Polymerization

2.3.1. Living ROMP

A catalyst solution was prepared by dissolving $\{RuCl_2(CHPh)[P(C_6H_{11})_3]_2\}$ (10 mg, 1.22×10^{-2} mmol) in 1 ml of anhydrous methylene chloride in an argon-filled drybox. The monomer CbzNB (0.665 g, 2.44×10^{-3} mol) was dissolved in 4 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 20 min. NBMPI (0.617 g, 2.44×10^{-3} mol) 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 NBMPI was added. The polymerization 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*-poly(NBMPI)-1, was precipitated in an excess of methanol and dried overnight in a vacuum system at room temperature to give a flaky white solid in essentially quantitative yield. Yield = 99.3%. The synthetic method of poly(CbzNB)-*b*-poly(NBMPI)-2 and poly(CbzNB)-*b*-poly(NBMPI)-3 were the same as poly(CbzNB)-*b*-poly(NBMPI)-1, except for the different amounts of CbzNB and NBMPI. All polymerizations are shown in Scheme 1.

2.3.2. Hydrogenation of poly(CbzNB)-b-poly(NBMPI)-1

Poly(CbzNB)-*b*-poly(NBMPI)-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 2,6-di-*tert*-butyl-4-methylphenol. 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



Scheme 1. Polymerization of diblock copolymers.

methanol. It was dissolved in methylene chloride and reprecipitated with methanol to further purify the white polymer. The hydrogenated polymer, hydrogenated poly(CbzNB)-*b*-poly(NBMPI)-1, was dried in vacuum overnight at room temperature. Yield = 98.8%. The synthetic method of hydrogenated poly(CbzNB)-*b*-poly(NBMPI)-2 and hydrogenated poly(CbzNB)-*b*-poly(NBMPI)-3 were the same as hydrogenated poly(CbzNB)-*b*-poly(NBMPI)-1.

2.4. Characterization methods

Thermogravimetric analysis (TGA) was measured on a Du Pont 2200 instrument at a heating rate of 20°C min^{-1} in air and 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 ($\overline{M}_n$) molecular weight were determined by gel permeation chromatography (GPC). Polystyrene was used as the standard. Four Waters (Ultrastyragel) columns 300 × 7.7 mm (500, 10^3, 10^4, 10^5 Å in 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 were recorded by a SHIMATSU RF-530 fluorescencemeter. ^{1}H 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. Polymerization and characterization of diblock copolymers

As the first stage, the living prepolymer of CbzNB was prepared by the polymerization with {$RuCl_2(CH\text{-}Ph)[P(C_6H_{11})_3]_2$} as catalyst, where the molar amount of CbzNB was 200 times that of the initiator ([CbzNB]/[initiator] = 200) and the polymerization was carried out at room temperature for 20 min. The number average molecular weight ($\overline{M}_n$) and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) were 58 000 and $\overline{M}_w/\overline{M}_n = 1.2$, respectively. The number average molecular weight was close to the

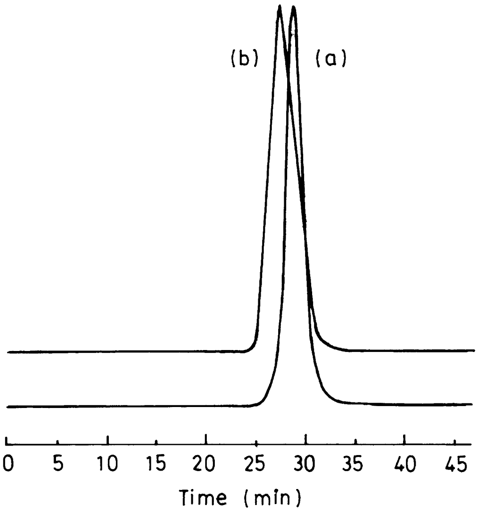


Fig. 1. GPC elution profiles (taken in THF at room temperature at a flow rate of 1.0 ml min^{-1}): (a) Poly(CbzNB) prepolymer, ([CbzNB]/[initiator] = 200); (b) poly(CbzNB)-*b*-poly(NBMPI)-1,([CbzNB]/[initiator] = 200; ([NBMPI]/[initiator] = 200)).

theoretical molecular weight calculated in accordance with [monomer]/[initiator] ratio ($\overline{M}_n = 54\,600$). For the polymerization of the second stage, NBMPI was added into the above reaction mixture and the polymerization was continued under polymerization conditions to similar those described above, where the molar amount of NBMPI was 200 times that of the initiator ([NBMPI]/[initiator] = 200). The number average molecular weight ($\overline{M}_n$) of polymer increased from 58 000 to 98 010, retaining a narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n = 1.35$). Fig. 1 shows typical GPC profiles of the resulting diblock copolymer [poly(CbzNB)-*b*-poly(NBMPI)-1] obtained an that of the corresponding prepolymers. The GPC profile of poly(CbzNB)-*b*-poly(NBMPI)-1 obtained after the second stage of polymerization clearly shifted toward the higher molecular weight region of the molecular weight distributions. Thus, the polymerization of NBMPI was initiated from the living end of poly(CbzNB) with very high efficiency to produce poly(CbzNB)-*b*-poly(NBMPI)-1 diblock copolymer. These results confirm the 'living polymerization' behavior of the polymerization of CbzNB with the $\{RuCl_2(CHPh)[P(C_6H_{11})_3]_2\}$. However, the larger number average molecular weight ($\overline{M}_n = 118\,590$) and broader molecular weight distributions ($\overline{M}_w/\overline{M}_n = 1.72$) will be obtained when NBMPI was used first before CbzNB. Therefore, all diblock copolymers were prepared by adding CbzNB first, then NBMPI.

The number average molecular weight ($\overline{M}_n$) and molecular weight distributions ($\overline{M}_w/\overline{M}_n$) of these unhydrogenated and hydrogenated diblock copolymers are shown in Table 1. From Table 1, the number average molecular weight of three unhydrogenated diblock copolymers are close to the theoretical molecular weight calculated in accordance with [monomer]/[initiator] ratio, and the molecular weight distributions remain narrow ($\overline{M}_w/\overline{M}_n = 1.5$). After hydrogenation, the number average molecular weights slightly increased; however, the molecular weight distributions still remained narrow.

The ^{1}H NMR spectra of poly(CbzNB)-*b*-poly(NBMPI)-1 and the corresponding hydrogenated polymer are shown in Fig. 2(a) and (b), respectively. As the polymerization proceeded, the vinylic proton peaks at 6.11 and 6.28 ppm for CbzNB; 6.06 and 6.15 ppm for NBMPI disappeared [13–14]. The ^{1}H NMR spectrum Fig. 2(a) of poly(CbzNB)-*b*-poly(NBMPI)-1 shows new vinyl protons in the range 4.7–5.7 ppm. These broad signals correspond to the vinyl protons of the double bond of the ring-opened polymer. Unfortunately, the ^{1}H and ^{13}C NMR spectra were very complex with many overlapping multiplets or broad unresolved peaks and it was not possible to interpret them in terms of microstructural detail, as is often possible for polymers produced by ROMP [17]. After hydrogenation, the resonances between 4.7 and 5.7 ppm completely disappeared; and the aromatic resonances between 7.07 and 7.95 for CbzNB and NBMPI still remained Fig. 1(b). This shows that the hydrogenated diblock copolymers are successfully obtained by using *p*-toluenesulfonylhydrazide as a reducing agent.

3.1.1. Fluorescence of diblock copolymers

Poly(CbzNB)-*b*-poly(NBMPI)-1, poly(CbzNB)-*b*-poly(NBMPI)-2, poly(CbzNB)-*b*-poly(NBMPI)-3 and their corresponding hydrogenated diblock copolymers could be poured into a 7 cm diameter glass culture dish from methylene chloride solution to yield optically clear films. Poly(CbzNB)-*b*-poly(NBMPI)-1 exhibited a strong carbazole

Table 1
Polymer yield, molecular weight and molecular weight distribution of diblock copolymers

Polymer code	Yield (%)	$\overline{M}_n$[a] (g mol^{-1})	$\overline{M}_{n(th)}$[b]	$\overline{M}_w/\overline{M}_n$[a]
Poly(CbzNB)-*b*-poly(NBMPI)-1	99.3	98 010	105 200	1.35
Hydrogenated poly(CbzNB)-*b*-poly(NBMPI)-1	98.8	110 150	–	1.44
Poly(CbzNB)-*b*-poly(NBMPI)-2	99.4	564 400	560 600	1.48
Hydrogenated poly(CbzNB)-*b*-poly(NBMPI)-2	99.2	565 000	–	1.54
Poly(CbzNB)-*b*-poly(NBMPI)-3	99.8	603 110	596 600	1.44
Hydrogenated poly(CbzNB)-*b*-poly(NBMPI)-3	99.5	609 910	–	1.52

[a] As determined by GPC in THF using polystyrene as a calibration standard.

[b] Calculated by $\overline{M}_{n(th)} = \{[\text{monomer}]/[\text{initiator}] \times \overline{M}_{n\ (\text{monomer})}\}$.

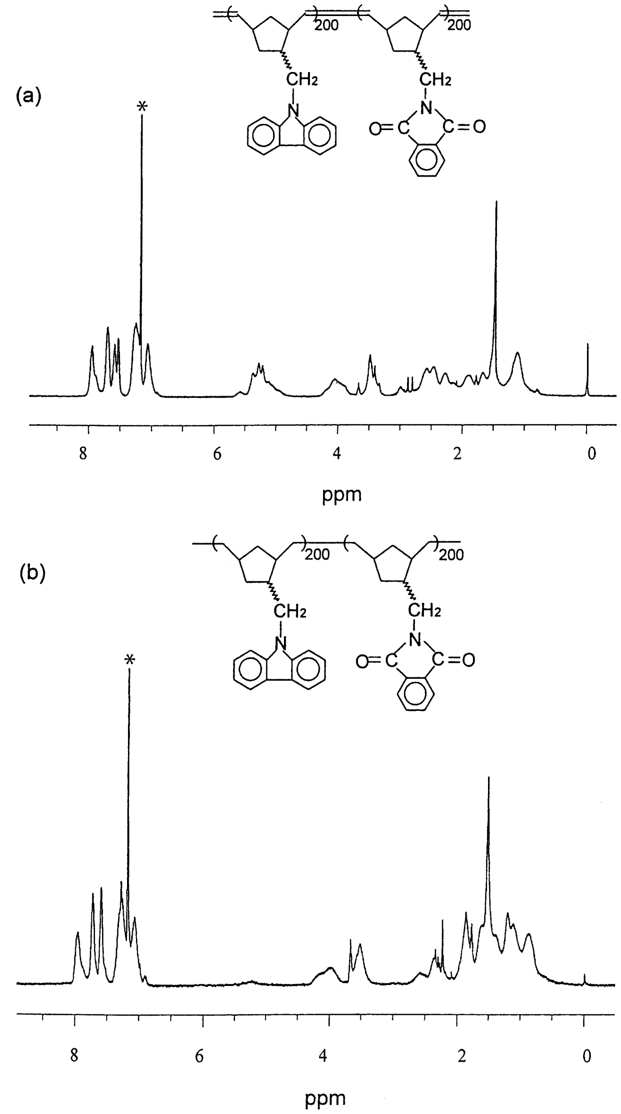


Fig. 2. ^{1}H NMR spectra of (a) poly(CbzNB)-*b*-poly(NBMPI)-1; (b) hydrogenated poly(CbzNB)-*b*-poly(NBMPI)-1. (Solvent: $CDCl_3$).

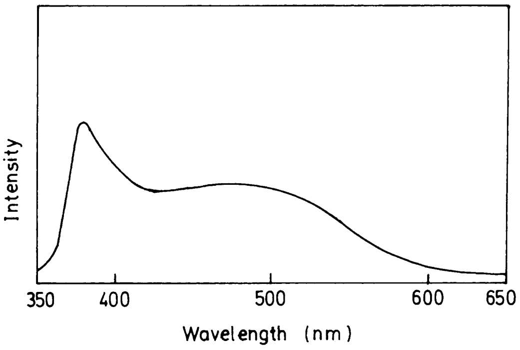


Fig. 3. Fluorescence emission spectra of poly(CbzNB)-*b*-poly(NBMPI)-1 (330 nm excitation).

fluorescence, with monomer emission occurring in the near-UV at approximately 380 nm and extending into the blue–violet region (Fig. 3) [13,18–19]. The spectra of poly(CbzNB)-*b*-poly(NBMPI)-2, poly(CbzNB)-*b*-poly(NBMPI)-3 and their corresponding hydrogenated diblock copolymers (not shown) were nearly identical to those of poly(CbzNB)-*b*-poly(NBMPI)-1, indicating that the electronic structure of the carbazole group is not greatly perturbed by the presence or absence of the second block, even after hydrogenation.

3.1.2. Solubility characteristics

The solubility characteristics of the diblock copolymers are shown in Table 2. It was found that there was no remarkable difference except in DMAc solvent between unhydrogenated and hydrogenated diblock copolymers. All diblock copolymers exhibited good solubility in a variety of solvents such as methylene chloride, chloroform, tetrahydrofuran, 1,2-dichlorobenzene, and even in *N*-methyl-2-pyrrolidinone and benzene at room temperature or upon heating to 60°C. The similar results were also observed in precious works for each homopolymer [13,15]. Each homopolymer and their

Table 2
Solubility of diblock copolymers in various solvents (Solubility: + + : soluble at room temperature; +: soluble at a heating temperature of 60°C; + − : partially soluble at 60°C; −: insoluble at 60°C; Abbreviations: THF: tetrahydrofuran; DMAc: *N*,*N*-dimethylacetamide; DMSO: dimethylsulfoxide; NMP: *N*-methyl-2-pyrrolidinone, DMF: *N*, *N*-dimethylformamide)

Polymer code	THF	DMAc	DMSO	1,2-Dichlorobenzene	NMP	Benzene	CH_2Cl_2	$CHCl_3$	DMF
Poly(CbzNB)-*b*-poly(NBMPI)-1	++	+	−	++	++	+	++	++	−
Hydrogenated poly(CbzNB)-*b*-poly(NBMPI)-1	++	+ −	−	++	++	+	++	++	−
Poly(CbzNB)-*b*-poly(NBMPI)-2	++	+	−	++	++	++	++	++	−
Hydrogenated poly(CbzNB)-*b*-poly(NBMPI)-2	++	+ −	−	++	++	++	++	++	−
Poly(CbzNB)-*b*-poly(NBMPI)-3	++	+	−	++	++	+	++	++	−
Hydrogenated poly(CbzNB)-*b*-poly(NBMPI)-3	++	+ −	−	++	++	+	++	++	−

Table 3
Thermal properties of the diblock copolymers

Polymer code	T_g[a] (°C)	$T_{d,10\%}$[b] (°C)	
		In air	In N_2
Poly(CbzNB)-*b*-poly(NBMPI)-1	144.1, 161.1	369	400
Hydrogenated poly(CbzNB)-*b*-poly(NBMPI)-1	131.2, 147.9	375	415
Poly(CbzNB)-*b*-poly(NBMPI)-2	146.5, 159.3	382	405
Hydrogenated poly(CbzNB)-*b*-poly(NBMPI)-2	126.3, 148.4	392	419
Poly(CbzNB)-*b*-poly(NBMPI)-3	147.5, 164.8	389	416
Hydrogenated poly(CbzNB)-*b*-poly(NBMPI)-3	133.1, 160.3	396	428

[a] Glass transition temperature (T_g) measured by DSC at a heating rate of 20°C min^{-1}.

[b] Temperatures at 10% mass loss ($T_{d,10\%}$) were determined by TGA at a heating rate of 20 °C min^{-1}.

hydrogenated homopolymer were all highly soluble in common organic solvents such as THF, chloroform and methylene chloride, but insoluble in DMSO and DMF [13,15]. Although the molecular weights of poly(CbzNB)-*b*-poly(NBMPI)-2 and poly(CbzNB)-*b*-poly(NBMPI)-3 are significantly higher than that of poly(CbzNB)-*b*-poly(NBMPI)-1, almost the same behaviors of solubility were observed.

3.1.3. Thermal stability

The thermal properties of the diblock copolymers were evaluated by differential scanning calorimetry (DSC) and TGA. The results are tabulated in Table 3. Glass transition temperature (T_g values) of diblock copolymers are summarized in Table 3. Phase separation occurs in all diblock copolymers, and two T_g values were observed. For example, poly(CbzNB)-*b*-poly(NBMPI)-1 had $T_g = 161.1$°C for CbzNB and $T_g = 144.1$°C for NBMPI, respectively. Also, two T_g values were still observed for hydrogenated diblock copolymers. For example, hydrogenated poly(CbzNB)-*b*-poly(NBMPI)-1 had $T_g = 147.9$°C for CbzNB and $T_g = 131.2$°C for NBMPI, respectively. However, lower T_g values were obtained after hydrogenation.

TGA was conducted in air and nitrogen atmospheres. The diblock copolymers were fairly stable up to a temperature around or above 370°C. The temperatures at 10% mass loss ($T_{d,10\%}$), as shown in Table 3, exhibited values ranging from 369 to 389°C in air and from 400 to 416°C in nitrogen for unhydrogenated diblock copolymers. However, hydrogenated diblock copolymers showed better thermal stability than unhydrogenated diblock copolymers, and the 10% weight loss temperatures were recorded in the range 375–396°C in air and 415–428°C in nitrogen. This indicated that hydrogenated ROMP diblock copolymers could enhance thermal stability, owing to the saturation of the double bond. From Table 3, the diblock copolymer with longer CbzNB segment before and after hydrogenation exhibited better thermal stability. Increasing the CbzNB moiety in a diblock copolymer, the thermal stability could be improved due to the characteristics of carbazole group in the diblock copolymer. In general, the incorporation of the carbazole group in a polymer backbone lead to enhanced thermal stability of the polymer [13,18,19]. The molecular weight of poly(CbzNB)-*b*-poly(NBMPI)-1 is significantly lower than those of poly(CbzNB)-*b*-poly(NBMPI)-2 and poly(CbzNB)-*b*-poly(NBMPI)-3. Poor thermostability was relatively observed for Poly(CbzNB)-*b*-poly(NBMPI)-1.

Furthermore, poly(NBMPI) and poly(CbzNB) homopolymers were prepared as described in precious works [13,15]. Poly(NBMPI) homopolymer ([NBMPI]/[initiator] = 400) showed near 398°C of the temperature at 10% weight loss ($T_{d,10\%}$) in nitrogen. Poly(CbzNB)-*b*-poly(NBMPI)-1 exhibited slightly higher temperature at 10% weight loss ($T_{d,10\%} = 400$°C) than poly(NBMPI) homopolymer ([NBMPI]/[initiator] = 400). Poly(CbzNB) homopolymer showed near 410°C of the temperature at 10% weight loss ($T_{d,10\%}$) in nitrogen. The temperature at 10% weight loss ($T_{d,10\%}$) of poly(CbzNB) homopolymer ([CbzNB]/[initiator] = 400) was higher than those of poly(CbzNB)-*b*-poly(NBMPI)-1 and Poly(NBMPI) homopolymer ([NBMPI]/[initiator] = 400).

4. Conclusions

Low polydispersity block copolymers of CbzNB and NBMPI have been synthesized via ROMP by using $\{RuCl_2(CHPh)[P(C_6H_{11})_3]_2\}$. Three diblock copolymers with CbzNB and NBMPI were made, varying both molecular weight and percent of each block. From ^{1}H NMR spectra, the ring-opened copolymers have predominantly trans double bonds. Their corresponding hydrogenated diblock copolymers were also successfully obtained. The molecular weight distributions of the diblock copolymers are narrow ($\overline{M}_w/\overline{M}_n \sim 1.5$). Hydrogenated and unhydrogenated diblock copolymers exhibited a strong carbazole fluorescence, with monomer emission occurring in the near-UV at approximately 380 nm and extending into the blue–violet region. All diblock copolymers exhibited good solubility; however, there is no remarkable difference between unhydrogenated and hydrogenated diblock copolymers. Two T_g values were observed for CbzNB segment and NBMPI segments before and after hydrogenation. Unhydrogenated diblock copolymers exhibited good thermal stability. However, hydrogenated diblock copolymers showed relatively better thermal stability than unhydrogenated diblock copolymers, owing to saturation of the main chain.

Acknowledgements

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References

[1] Grubbs RH, Tumas W. Science 1989;243:907.
[2] Schrock RR. Acc Chem Res 1990;23:158.
[3] Novak BM, Grubbs RH. J Am Chem Soc 1988;110:7542.
[4] Feast WJ. Makromol Chem, Macromol Symp 1992;53:317.
[5] Risse W, Grubbs RH. J Mol Catal 1991;65:211.
[6] Vannikov AV, Grishina AD. Photochemistry of polymer donor–aceptor complexes. Moscow: Nauka, 1984.
[7] Schaffert RM. IBM J Rev Dev 1975;15:75.
[8] Naarmann H, Strohriegel D. In: Kricheldorf HR, editor. Handbook of polymer synthesis. New York: Marcel Dekker, 1992. p. 1404.
[9] Park JW, Lee JH, Cho HN, Choi SK. Macromolecules 1986; 19:521.
[10] Helary G, Chevrot C, Sauvet G, Siove A. Polym Bull 1991;26:131.
[11] Lee JH, Park JW, Ko JM, Chang YH, Choi SK. Polym Bull 1993;31:339.
[12] Gratt J, Cohen RE. Macromolecules 1997;30:3137.
[13] Liaw DJ, Tsai CH. J Mol Catal A 1999;147:23.
[14] Liaw DJ, Wu PL, Huang CC. Macromol Symp 2000;150:313.
[15] Liaw DJ, Tsai CH. Polymer 2000;41:2773.
[16] Liaw DJ, Tsai JS, Wu PL. Macromolecules 2000;33:6925.
[17] Ivin KJ, Mol H. Olefin metathesis and metathesis polymerization. New York: Academic Press, 1997.
[18] Gratt J, Cohen RE. Macromolecules 1997;30:3137.
[19] Liaw DJ, Wu PL. J Mol Catal A 2000;160:35.