Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 47 (2006) 3057–3064

polymer

www.elsevier.com/locate/polymer

# Novel fluorescent polynorbornenes with multi-functional armed structure by using highly stable block macroinitiators via a combination of living ring-opening metathesis polymerization and atom transfer radical polymerization

Der-Jang Liaw [a,*], Ching-Cheng Huang [a], En-Tang Kang [b]

[a] Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, Keelung Road, Section 4, Taipei 106, Taiwan
[b] Department of Chemical and Biomolecular Engineering, National University of Singapore Kent Ridge, Singapore 119260

Received 8 December 2005; received in revised form 8 February 2006; accepted 13 February 2006
Available online 20 March 2006

**Abstract**

Novel organosoluble fluorescent polynorbornenes with multi-functional armed structure were designed and prepared by using highly stable block macroinitiators via a combination of living ring-opening metathesis polymerization (ROMP) and atom transfer radical polymerization (ATRP). A bromo-containing functional norbornene (NBMBr) was prepared from the Diels–Alder reaction of cyclopentadiene and allyl bromide. The diblock copolymer of 5-(*N*-carbazolyl methyl)bicycle[2.2.1]hept-2-ene (CbzNB) and NBMBr was successfully prepared using living ROMP and used as a novel macroinitiator [poly(CbzNB-*b*-NBMBr)] for ATRP. Carbazoyl-containing multi-functional armed copolymer with poly(methyl methacrylate) (PMMA) was prepared by using poly(CbzNB-*b*-NBMBr) as a macroinitiator for ATRP. Strong fluorescence emissions (370–450 nm) were observed in the low excimer-forming multi-functional armed fluorescent polynorbornenes. The fact is that low excimer-forming carbazole-containing polymeric compound would apparently be favorable in photoconductive materials. The multi-functional armed structure make this compound an attractive candidate for applications as multi-modified hole transport materials in molecular electronic devices. Multi-modification could be further considered to be carried out by using such a functional bromo group at the end of multi-arms.

*Keywords:* Ring-opening metathesis polymerization; Atom transfer radical polymerization; Macroinitiator

## 1. Introduction

Controlled-polymerization techniques have been adopted to prepare well-defined polymers with controlled molecular weight, polydispersities and terminal functionalities [1–7]. These techniques can be proceeded by anionic, cationic, group transfer, Ziegler–Natta, radical mechanism, atom transfer radical polymerization (ATRP), ring-opening metathesis polymerization (ROMP) or metathesis polymerization [5–12]. Of particular interest today is a combination of the two of these processes for the formation of new polymeric materials [13–19]. There has been an increasing interest in developing the synthesis of macromolecules with novel branched architectures, which involve star-branched, star-linear block, dendrimer–linear block, comblike, macrocyclic comblike, brushlike star, dendrigraft, and dendrimer-like branched polymers [13–19].

Carbazole-functionalized bicycle[2.2.1]hept-2-ene derivatives have recently been polymerized using classical, olefin metathesis catalysts such as $RuCl_3$ and $RuCl_2(PPh_3)_3$ [20]. The resulting homopolymer was reported to exhibit interesting properties such as electro optical properties and thermal stability [21,22]. In our previous works, we have successfully synthesized 5-(*N*-carbazolyl methyl)bicycle[2.2.1]hept-2-ene (CbzNB) and prepared their polymers via living ROMP [21,22]. Incorporation of the carbazoyl group enhanced the thermal stability of the polymers and provided better electro-optical properties to the polymers [20–22].

Synthesis of the polymers with well-defined structures is among the central subjects in polymer chemistry. The polymers bearing multiple end-functionality, which is capable of initiating graft copolymerization, allow the combination of mechanistically compatible or incompatible polymerization

---

[*] Corresponding author. Tel.: +886 2 2737 6638/886 2 2733 5050; fax: +886 2 2737 6644/886 2 2378 1441.

*E-mail addresses:* liaw@ch.ntust.edu.tw (D.-J. Liaw), liaw8484@yahoo.com.tw (D.-J. Liaw).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.02.023

processes, leading to a variety of multi-armed block copolymers with well-defined structures. The present study provides a new synthetic route for building novel carbazoyl-containing block polymer structures based on living ROMP and ATRP. Another novelty in the present study is the synthesis of carbazoyl-containing macroinitiator [poly(CbzNB-*b*-NBMBr)] for ATRP by living ROMP using Ru catalyst (I) $\{RuCl_2(CHPh)[P(C_6H_{11})_3]_2\}$. ATRP was employed to grow the PMMA (polymethyl methacrylate) side chains from the backbone of poly(CbzNB-*b*-NBMBr) because of the incorporation of functional alkyl bromide group. Carbazoyl-containing grafted copolymer with PMMA, poly[(CbzNB-*b*-NBMBr)-*g*-PMMA] was obtained. This is the first ever attempt to prepare carbazoyl-containing diblock polymeric material, a novel organosoluble functional fluorescent material, by the combination of living ROMP and ATRP techniques. Further, the hydrogenated diblock copolymer, poly(HCbzNB-*b*-HNBMBr), was obtained by using *p*-toluenesulfonylhydrazide as a reducing agent. Characterization of poly(CbzNB-*b*-NBMBr), poly(HCbzNB-*b*-HNBMBr) and poly[(CbzNB-*b*-NBMBr)-*g*-PMMA] such as $^1H$ NMR and fluorescence emission behavior of the polymers was also investigated.

## 2. Experimental

### 2.1. Materials

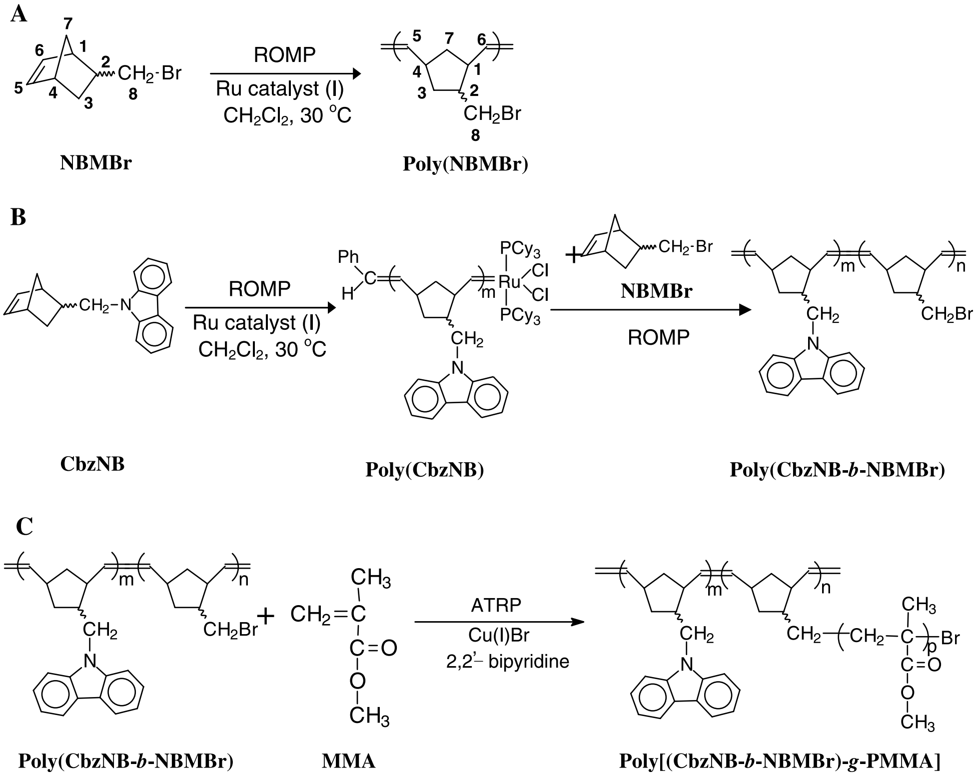
The ligand for ATRP such as 2,2′-bipyridine (Merck) was used as received without purification. Cu(I)Br (98%, Acros) was purified by washing with glacial acetic acid, followed by absolute ethanol and ethyl ether, and then dried under vacuum. Solvents and methyl methacrylate (Merck) were purified by standard procedures. The monomer of 5-(*N*-carbazoyl methyl)-bicycle[2.2.1]hept-2-ene (CbzNB) was prepared as described before (mp = 74–76 °C) [21].

### 2.2. Preparation of norbornyl-containing initiator for ATRP

Bromo- and norbornyl containing 5-(bromo methyl)bicycle[2.2.1]hept-2-ene (NBMBr) (bp = 76–78 °C/13 mm Hg) for atom transfer radical polymerization (ATRP) was synthesized by Diels–Alder reaction of cyclopentadiene and allyl bromide. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) = 6.19 ($H_{n5}$), 6.15–6.16 ($H_{x5}$ and $H_{x6}$), 5.89 ($H_{n6}$), 3.38 ($H_{x8}$), 3.20 ($H_{n8}$) 2.99–3.04 ($H_{n4}$, $H_{n1}$ and $H_{x1}$), 2.85 ($H_{x4}$), 2.50 ($H_{n2}$), 1.92 ($H_{n3x}$), 1.78 ($H_{x2}$), 1.48 ($H_{n7s}$), 1.35 ($H_{x7s}$, $H_{x7a}$ and $H_{x3n}$), 1.27 ($H_{n7a}$), 1.21 ($H_{x3x}$) and 0.58 ($H_{n3n}$). $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ (ppm) = 138.13 ($C_{n5}$), 137.47 ($C_{x5}$), 136.94 ($C_{x6}$), 132.23 ($C_{n6}$), 50.27 ($C_{n7}$), 48.03 ($C_{n1}$), 45.12 ($C_{x4}$), 44.88 ($C_{x1}$), 43.06 ($C_{n4}$), 42.03 ($C_{n2}$), 41.13 ($C_{x2}$), 39.10 ($C_{x8}$), 38.14 ($C_{n8}$), 33.28 ($C_{x3}$) and 32.74 ($C_{n3}$).

### 2.3. Preparation of carbazoyl-containing macroinitiator via ROMP using catalyst (I) $\{RuCl_2(CHPh)[P(C_6H_{11})_3]_2\}$

The high functional group tolerance of Ru catalyst (I) has prompted to investigate the polymerization of functional NBMBr by ROMP in the formation of novel macroinitiators



Scheme 1. (A) Polymerization of NBMBr using Ru catalyst (I); (B) preparation of carbazoyl-containing macroinitiator via living ROMP; and (C) preparation of poly[(CbzNB-*b*-NBMBr)-*g*-PMMA].

for ATRP. NBMBr (2.5 mmol) was dissolved in 4 mL of methylene chloride. After a freeze–pump–thaw cycle, the solution of Ru catalyst (I) ($2.5\times10^{-3}$ mmol) in 1 mL of methylene chloride was injected to the monomer solution. The solution was stirred for 2 h at 30 °C. The reaction was terminated by the addition of a trace amount of ethyl vinyl ether (0.1 mL). The solution was continuously stirred for another 10 min, and then the polymer was precipitated in excess of methanol and filtered. Poly(NBMBr) was thus obtained (Scheme 1(A)). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) = 5.15–5.65 ($H_5$ and $H_6$), 3.21–3.61 ($H_8$), 0.85–3.20 ($H_1$, $H_2$, $H_3$, $H_4$ and $H_7$) (Scheme 1(A)). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ (ppm) = 127.55–136.45 ($C_5$ and $C_6$), 35.25–49.00 ($C_1$, $C_2$, $C_3$, $C_4$, $C_7$ and $C_8$) (Scheme 1(A)). Polymerization of the monomer, CbzNB, can be carried out by living ROMP [21,22]. The new macroinitiator, poly(CbzNB-*b*-NBMBr), for ATRP was synthesized via living ROMP (Scheme 1(B)). A solution of catalyst was prepared by dissolving $\{RuCl_2(CHPh)[P(C_6H_{11})_3]_2\}$ ($1.22\times10^{-2}$ mmol) in 1 mL of anhydrous methylene chloride under an argon-filled drybox. The monomer CbzNB ($9.8\times10^{-3}$ 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 using a syringe. The pink solution was vigorously stirred for 2 h at 30 °C. NBMBr ($1.22\times10^{-3}$ mol) was injected to the still-living reaction mixture and the reaction mixture was stirred for another 12 h at 30 °C. The color of the solution changed from pink to yellow after the addition of NBMBr. 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 mm and poly(CbzNB-*b*-NBMBr) was precipitated in excess of methanol and the polymer was filtered and dried overnight in a vacuum system at ambient temperature. A flaky white solid was obtained [Scheme 1(B)]. The structure of poly(CbzNB-*b*-NBMBr) was conformed by $^1$H NMR spectroscopy (Fig. 1(A)). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ (ppm) = 107.84–143.53 ($C_5$, $C_{5'}$, $C_6$, $C_{6'}$ and $C_9$), 28.27–46.98 ($C_1$, $C_{1'}$, $C_2$, $C_{2'}$, $C_3$, $C_{3'}$, $C_4$, $C_{4'}$, $C_7$, $C_{7'}$, $C_8$ and $C_{8'}$) (Scheme 1(B), Fig. 1(A)).

### 2.4. Preparation of a grafted copolymer with PMMA derived from the carbazoyl-containing macroinitiator via ATRP

The ligand for ATRP such as 2,2′-bipyridine (Merck) was used as received without purification. CuBr (98%, Acros) was purified by washing with glacial acetic acid, followed by absolute ethanol and ethyl ether, and then dried under vacuum. To an ampoule, Cu(I)Br (0.143 g, 1 mmol), 2,2′-bipyridine (0.156 g, 1 mmol), poly(CbzNB-*b*-NBMBr), [$\bar{M}_n = 3.2\times10^4$, $\bar{M}_w/\bar{M}_n = 1.5$] (0.5 g), methyl methacrylate (MMA) (1 g, 10 mmol) and 50 mL toluene were added. The heterogeneous mixture was placed under vacuum and then degassed via a freeze–pump–thaw cycle thrice. After complete degassing, the ampoule was stirred at 100 °C for 12 h. The polymer was precipitated from methanol; dissolved in THF and reprecipitated from methanol three times. The molecular weight of poly[(CbzNB-*b*-NBMBr)-*g*-PMMA] was obtained as $3.5\times10^5$ by NMR (Scheme 1(C)). The structure of

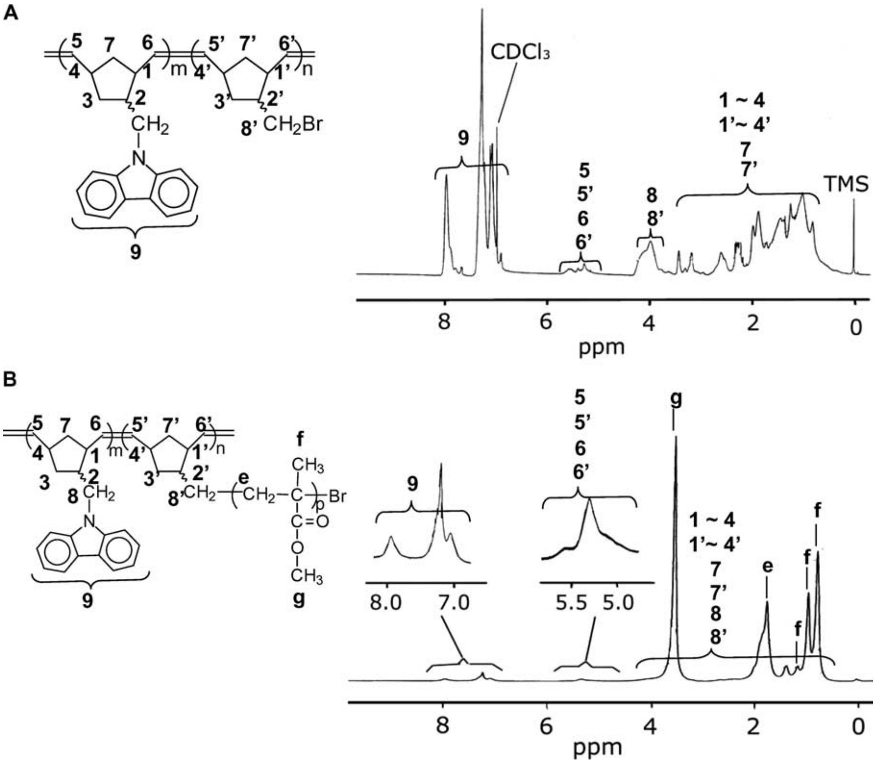


Fig. 1. (A) 400 MHz $^1$H NMR spectrum ($CDCl_3$, 25 °C) of poly(CbzNB-*b*-NBMBr) and (B) 400 MHz $^1$H NMR spectrum ($CDCl_3$, 25 °C) of poly[(CbzNB-*b*-HNBMBr)-*g*-PMMA].

poly[(CbzNB-*b*-NBMBr)-*g*-PMMA] was confirmed by $^1$H NMR spectroscopy (Fig. 1(B)).

### 2.5. Hydrogenation of the carbazoyl-containing macroinitiator

Poly(CbzNB-*b*-NBMBr) (0.5 g) was dissolved in 50 mL of xylene in an ampoule. To the above solution 2.75 g (ca. 7.5 equiv. relative to the repeating unit) of *p*-toluenesulfonylhydrazide was added as a hydrogenation agent with a trace of 2,6-di-*tert*-butyl-4-methylphenol were added. The ampoule containing the polymer, solvent and hydrogenation agent was then degassed thrice via a freeze–pump–thaw cycle and sealed. The ampoule was gradually heated to 120 °C. A homogeneous solution resulted at 100 °C. The solution was stirred at 120 °C for 4 h until the generation of gas bubbles ceased. The solution was cooled to room temperature and precipitated from methanol. The polymer was purified by reprecipitation from methanol. Hydrogenated poly(CbzNB-*b*-NBMBr)[poly(HCbzNB-*b*-HNBMBr)] was dried by freeze–drying in benzene. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) = 6.88–7.95 ($H_9$), 0.08–4.20 ($H_1$, $H_{1'}$, $H_2$, $H_{2'}$, $H_3$, $H_{3'}$, $H_4$, $H_{4'}$, $H_5$, $H_{5'}$, $H_6$, $H_{6'}$, $H_7$, $H_{7'}$, $H_8$ and $H_{8'}$) (Scheme 2(A)). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ (ppm) = 108.88–140.41 ($C_9$), 28.27–47.10 ($C_1$, $C_{1'}$, $C_2$, $C_{2'}$, $C_3$, $C_{3'}$, $C_4$, $C_{4'}$, $C_5$, $C_{5'}$, $C_6$, $C_{6'}$, $C_7$, $C_{7'}$, $C_8$ and $C_{8'}$) (Scheme 2(A)).

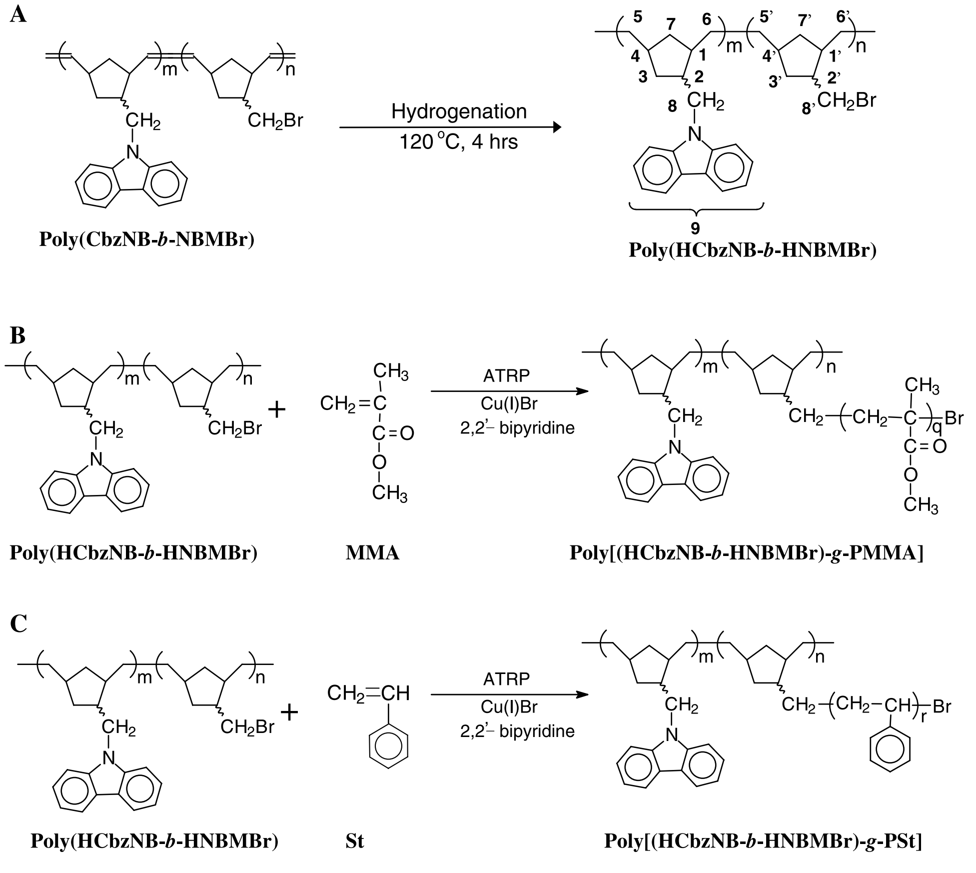
### 2.6. Instruments

$^1$H NMR and $^{13}$C NMR spectra were taken on a JEOL EX-400 spectrometer operating at 399.65 MHz for proton and 100.40 MHz for carbon. Weight-average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weights were determined by gel permeation chromatography (GPC) at room temperature. Polystyrene was used as the standard. Four Waters (Ultrastyragel) columns 300 mm × 7.8 mm (500, $10^3$, $10^4$, $10^5$ 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 spectra were recorded by a Shimadzu RF-5031 spectrophotometer. All the fluorescence measurements were performed at room temperature by excitation at 330 nm wavelength.

## 3. Results and discussion

### 3.1. Synthesis and characterization of new macroinitiators via living ROMP

Matyjaszewski et al. reported that one of the demerits of using atom transfer radical polymerization (ATRP) to grow the side chains from the backbone is that radical–radical coupling may lead to cross-linked polymers or polymers with multimodal molecular weight distributions [7,23]. When



Scheme 2. (A) Hydrogenation of poly(CbzNB-*b*-NBMBr); (B) preparation of poly[(HCbzNB-*b*-HNBMBr)-*g*-PMMA]; (C) preparation of poly[(HCbzNB-*b*-HNBMBr)-*g*-PSt].

the macroinitiators were prepared with high efficiency initiation sites for ATRP and tried to get grafted copolymer with methyl methacrylate (MMA) or styrene (St), gel formation was observed during the ATRP because of high initiation efficiency of the macroinitiators [7,23]. The grafted copolymers with polymethyl methacrylate were insoluble in common organic solvents and was presumed to be highly cross-linked due to radical–radical coupling of the side chain [7,23]. A similar phenomenon was discussed by Matyjaszewski et al. in the graft copolymerization of poly(2-(2-bromopropionyloxy)ethyl methacrylate) macroinitiator [pBIEM] [7,23]. To avoid this problem of cross-linked reaction, the diblock copolymeric macroinitiators of CbzNB and NBMBr with low initiation efficiency of initiation site were designed and synthesized as macroinitiators to prevent the termination by radical-radical coupling as much as possible during polymerization [7,23]. The R-$CH_2$–Br within the macroinitiator is not the common high efficiency initiation site for ATRP because the formed radical, –$CH_2\cdot$, has no resonance or conjugation from the substitutents to stabilize the formed radical, which will result in a low grafting efficiency. Specifically, the low efficiency initiation site is good for preparation of desired and organosoluble grafted polynorbornenes to avoid cross-linking of the side chain. Hence, the organosoluble diblock polymeric material containing carbazoyl groups were easily obtained via a combination of living opening metathesis polymerization and atom transfer radical polymerization. In addition, the diblock copolymers of CbzNB and NBMBr were designed to avoid high steric hindrance in comparison with the random copolymers of CbzNB and NBMBr. So diblock copolymers of CbzNB and NBMBr can provide relatively effective initiation of the initiation site from polyNBMBr segments compared with random copolymers of CbzNB and NBMBr. Atom transfer radical polymerization (ATRP) of long chain polyNBMBr segments can be carried out easily because there is almost no bulky carbazoyl group near initiation site of polyNBMBr segments within diblock copolymers of CbzNB and NBMBr.

New organosoluble and highly stable macroinitiators containing fluorescent pendant groups were prepared via living ring-opening metathesis polymerization (ROMP). A functional norbornene, NBMBr, was synthesized by Diels–Alder reaction. After living ROMP of CbzNB and NBMBr, poly(CbzNB-*b*-NBMBr) containing alkyl bromide group was obtained (Scheme 1(B)). Atom transfer radical polymerization (ATRP) could be considered by using the alkyl bromide of side chain within poly(CbzNB-*b*-NBMBr). In the $^1$H NMR spectrum of poly(CbzNB-*b*-NBMBr) (Fig. 1(A)), as the vinylic proton peaks of norbornene ring of NBMBr or CbzNB at about $\delta$ 5.90 and 6.00 ppm disappeared, the polymer showed new and broad signals due to vinyl protons as between $\delta$ 5.10 and 5.80 ppm (Fig. 1(A)). After hydrogenation, the resonances between $\delta$ 5.10 and 5.80 ppm completely disappeared; and the aromatic resonances between $\delta$ 6.80 and 8.10 ppm for CbzNB still remained. It confirmed the successful hydrogenation of the diblock copolymers by *p*-toluenesulfonylhydrazide [6]. This is the first ever attempt to prepare saturated diblock polymeric material containing carbazole group, a novel organosoluble functional fluorescent material, which could be used as a novel macroinitiator for ATRP.

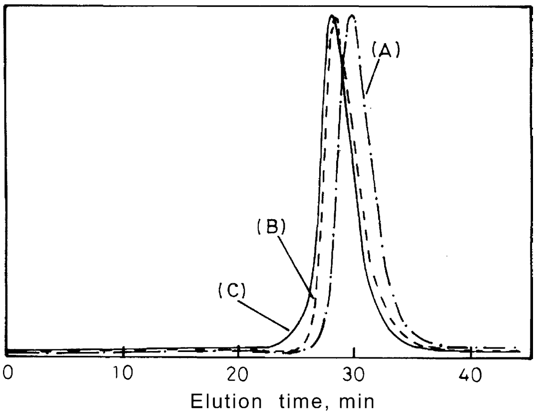


Fig. 2. GPC elution profiles (in THF at room temperature at a flow rate of 1.0 mL min$^{-1}$): (A) poly(CbzNB) prepolymer, (B) poly(CbzNB-*b*-NBMBr), and (C) poly[(CbzNB-*b*-NBMBr)-*g*-PMMA].

As the first stage, the living prepolymer of CbzNB was prepared by the polymerization with $\{RuCl_2(CHPh)[P(C_6H_{11})_3]_2\}$ as catalyst, where the molar amount of CbzNB was 80 times that of the initiator ([CbzNB]/[initiator] = 80) and the polymerization was carried out at 30 °C for 2 h (Scheme 1(B)). The number average molecular weight ($\bar{M}_n$) of poly(CbzNB) was $2.2\times10^4$ (Fig. 2(A)) (the molecular weight was theoretically calculated in accordance with [CbzNB]/[initiator] ratio; $Mn_{th}=2.2\times10^4$). For the polymerization of the second stage, NBMBr was added to the above reaction mixture [poly(CbzNB) solution] and the reaction was continued under similar conditions as of the above, where the molar amount of NBMBr was 100 times that of the initiator ([NBMBr]/[initiator] = 100) (Scheme 1(B)). The number average molecular weight ($\bar{M}_n$) of polymer increased from $2.2\times10^4$ [poly(CbzNB)] to $3.2\times10^4$ [poly(CbzNB-*b*-NBMBr)] (Fig. 2(B)). Typical GPC profiles of the resulting diblock copolymer [poly(CbzNB-*b*-NBMBr)] and that of the corresponding prepolymer were observed. The GPC profile of poly(CbzNB-*b*-NBMBr) obtained after the second stage of polymerization clearly shifted toward the higher molecular weight region. Thus, polymerization of NBMBr was initiated from the living end of poly(CbzNB) with very high efficiency to produce poly(CbzNB-*b*-NBMBr) diblock copolymer (Scheme 1(B)). These results confirm the 'living polymerization' behavior of the polymerization of CbzNB with the $\{RuCl_2(CHPh)[P(C_6H_{11})_3]_2\}$.

### 3.2. Synthesis and characterization of new branched functional polynorbornenes via ATRP

Poly(CbzNB-*b*-NBMBr) was used as a macroinitiator for ATRP to prepare the branched copolymer with MMA (methyl methacrylate) (Scheme 1(C)). As the *graft*-copolymerization with MMA of poly(CbzNB-*b*-NBMBr) proceeded, the appearance of signals due to grafted PMMA segments in the $^1$H NMR spectrum of the polymer confirmed the formation of the

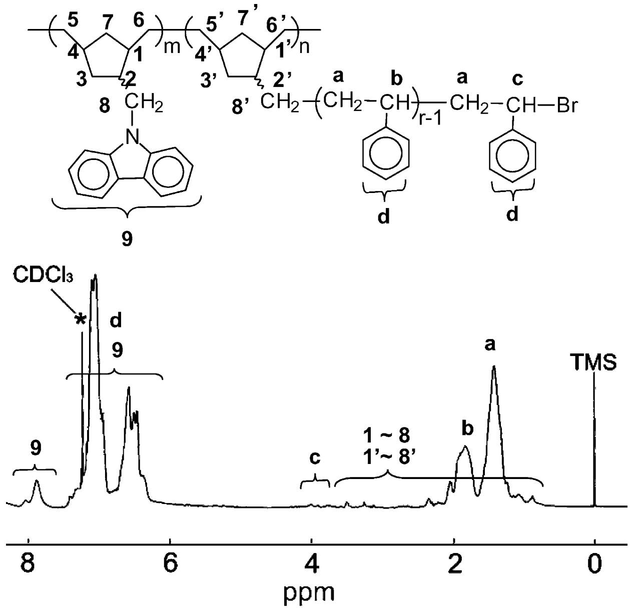


Fig. 3. 400 MHz $^1$H NMR spectrum (CDCl$_3$, 25 °C) of poly[(HCbzNB-*b*-HNBMBr)-*g*-PSt].

branched poly[(CbzNB-*b*-NBMBr)-*g*-PMMA] (Fig. 1(B)). In the $^1$H NMR spectrum of poly[(CbzNB-*b*-NBMBr)-*g*-PMMA] (Fig. 1(B)), signals of low intensity characteristic of the vinylic protons of norbornene ($\delta$ 4.90–5.70 ppm) were observed along with those of olefin region ($\delta$ 1.0–4.2 ppm) and PMMA segment [$\mathrm{–C}H_2\mathrm{C(CH_3)COOCH_3}$ $\delta$ 1.90 ppm; $\mathrm{–CH_2C(C}H_3\mathrm{)}$-$\mathrm{COOCH_3}$: $\delta$ 0.87, 1.04, 1.70 ppm; $\mathrm{–CH_2C(CH_3)COOC}H_3$: $\delta$ 3.60 ppm] were observed (Fig. 1(B)). The experimental average molecular weight ($\bar{M}_n$) of $3.5\times10^5$ for poly[(CbzNB-*b*-NBMBr)-*g*-PMMA] was calculated from the relative intensity of the aromatic and other protons (olefin region and PMMA segment) of NMR and GPC. The composition of poly[(CbzNB-*b*-NBMBr)-*g*-PMMA] was calculated from NMR ($m\sim80$, $n\sim53$, and $p\sim60$ by NMR; Scheme 1(B)). *Block* and *graft* copolymer, poly[(CbzNB-*b*-NBMBr)-*g*-PMMA] with multi-functional armed structure was obtained and this compound could be considered as an attractive candidate for applications such as hole transport materials in molecular electronic devices. Furthermore, multi-modification could be considered to be carried out by using such functional bromo group at the end of multi-arms.

Hydrogenated macroinitiator of poly(HCbzNB-*b*-HNBMBr) ($\bar{M}_n = 3.2\times10^4$) (Fig. 2(C)) could be used for the preparation of branched poly[(HCbzNB-*b*-HNBMBr)-*g*-PMMA]. The $\bar{M}_n$ of branched poly[(HCbzNB-*b*-HNBMBr)-*g*-PMMA] was $3.9\times10^5$ higher than that of poly(HCbzNB-*b*-HNBMBr) ($\bar{M}_n = 3.2\times10^4$) (Scheme 2(B)). In addition, branched poly[(HCbzNB-*b*-HNBMBr)-*g*-PSt] could be prepared by using hydrogenated macroinitiator of poly(HCbzNB-*b*-HNBMBr) ($\bar{M}_n = 3.2\times10^4$). Branched poly[(HCbzNB-*b*-HNBMBr)-*g*-PSt] with $\bar{M}_n = 4.1\times10^5$ was obtained and characterized by $^1$H NMR (Fig. 3) (Scheme 2(C)). The characteristic low intensity of the signals was associated with olefin region (1.0–4.2 ppm) whereas the strong intensity of the signals associated with polystyrene (PSt) segment [$\mathrm{–C}H_2$-$\mathrm{C(H)(C_6H_5)–}$: 1.20–1.70 ppm; $\mathrm{–CH_2C(}H\mathrm{)(C_6H_5)–}$: 1.80–2.50 and 4.0–4.2 ppm; $\mathrm{–CH_2C(H)(C_6}H_5\mathrm{)–}$: 6.3–7.6 ppm] were observed ($m\sim80$, $n\sim53$, and $r\sim69$ by NMR; Scheme 2(C)) (Fig. 3).

### 3.3. Fluorescence emissions of poly(CbzNB-b-NBMBr), poly(HCbzNB-b-HNBMBr) and poly[(CbzNB-b-NBMBr)-g-PMMA]

The methyl methacrylate (MMA) and styrene are common monomers for ATRP. Also they are easy to be controlled to prepare grafted polynorbornenes by ATRP. In this study, the introducing polyMMA or polystyrene chain into the

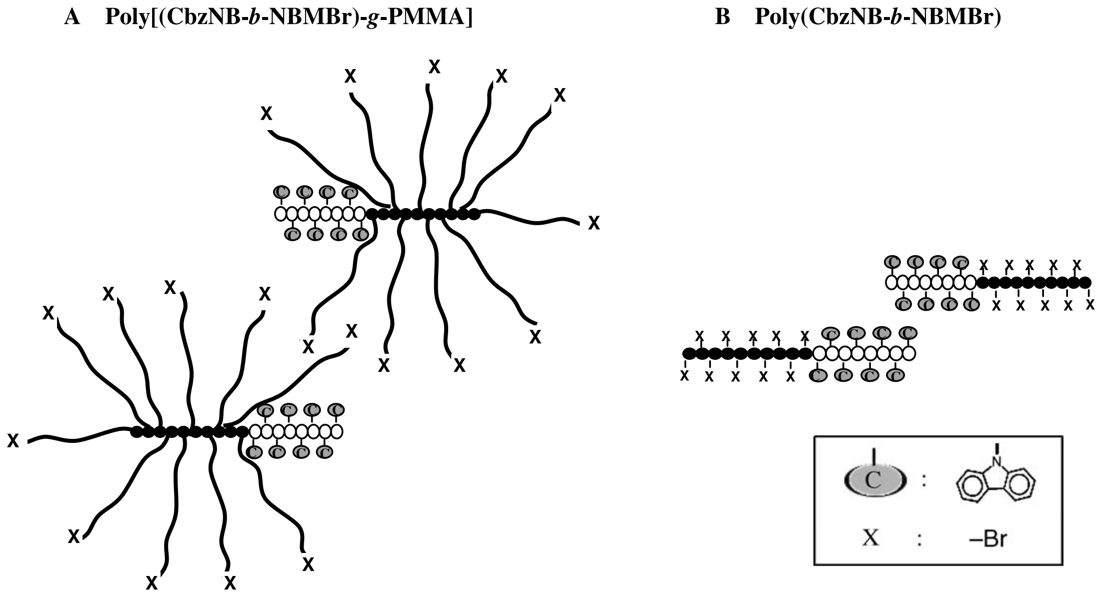

**A Poly[(CbzNB-*b*-NBMBr)-*g*-PMMA]** **B Poly(CbzNB-*b*-NBMBr)**

Fig. 4. Proposed model of fluorescent properties of (A) poly(CbzNB-*b*-NBMBr) and (B) poly[(CbzNB-*b*-NBMBr)-*g*-PMMA].

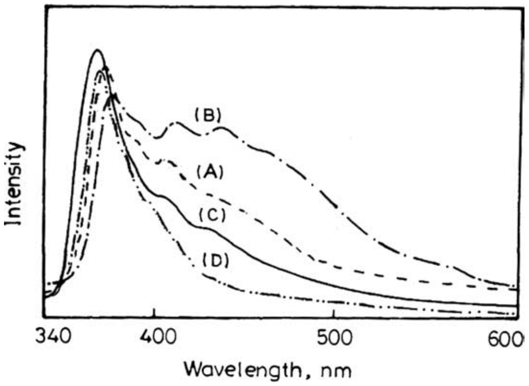


Fig. 5. Fluorescence emission spectra of (A) poly(CbzNB-*b*-NBMBr), (B) poly(HCbzNB-*b*-HNBMBr), (C) poly[(CbzNB-*b*-NBMBr)-*g*-PMMA] and (D) poly(SCbzNB-*b*-NBMBr). (330 nm excitation).

carbazole-containing polymer could be employed as the polymeric brush to avoid excimer formation (Fig. 4(A)).

Poly(CbzNB-*b*-NBMBr) exhibited a strong carbazole fluorescence, with monomer emission occurring in the near-UV at approximately 380 nm and extending into the blue–violet region (Fig. 5(A)). A low-level emission observed at higher wavelengths (480 nm) was probably due to excimer formation. Also, strong carbazole emissions (370–500 nm) were observed in the fluorescence spectra of poly(CbzNB-*b*-NBMBr) (Fig. 5(A)), poly(HCbzNB-*b*-HNBMBr) (Fig. 5(B)) and poly[(CbzNB-*b*-NBMBr)-*g*-PMMA] (Fig. 5(C)). In the spectra of poly(CbzNB-*b*-NBMBr) (Fig. 5(A)), its corresponding hydrogenated diblock copolymer [poly(HCbzNB-*b*-HNBMBr)] (Fig. 5(B)) and its corresponding branched poly[(CbzNB-*b*-NBMBr)-*g*-PMMA] (Fig. 5(C)) indicated that the electronic structure of the carbazole group was not greatly perturbed by the presence or absence of the second block even after hydrogenation and graft copolymerization. The mobility and flexibility of the main chain of hydrogenated poly(CbzNB-*b*-NBMBr)[poly(HCbzNB-*b*-HNBMBr)] was increased because of the saturation of the double bonds, which facilitates the formation of the excimer. After *graft* copolymerization of poly(CbzNB-*b*-NBMBr) with MMA (Scheme 1(C)), the carbazole groups were buried in the PMMA chains of poly[(CbzNB-*b*-NBMBr)-*g*-PMMA], the carbazole groups were placed apart, and the excimer formation decreased (Fig. 4) [24,25]. Strong fluorescence emissions (370–450 nm) were observed in the low excimer-forming multi-functional armed poly[(CbzNB-*b*-NBMBr)-*g*-PMMA]. The fluorescence emission with narrow distribution (370–450 nm) could be observed (Fig. 5(C)). Furthermore, the distribution of fluorescence emission would depend on the mole fraction of polyNBMBr as well as polyMMA in the copolymers. Poly(CbzNB-*b*-NBMBr) with short poly(CbzNB) segment also was prepared and referred to as poly(SCbzNB-*b*-NBMBr) ($m=20$ and $n=100$) hereafter (Scheme 1(B)). Strong carbazole fluorescence emissions (370–500 nm) were observed in the fluorescence spectrum of poly(SCbzNB-*b*-NBMBr) (Fig. 5(D)). However, carbazole dimer of poly(SCbzNB-*b*-NBMBr) was more difficult to form than that of poly(CbzNB-*b*-NBMBr) with long poly(CbzNB) segment. That is, smaller amount of carbazole group incorporated into the diblock copolymer would avoid the population of excimer formation. In this study, the composition of poly[(CbzNB-*b*-NBMBr)-*g*-PMMA] was calculated from NMR ($m\sim80$, $n\sim53$, and $p\sim60$ by NMR; Scheme 1(B)), which is the optimal mole fraction of polyNBMBr in the block copolymer as well as polyMMA in the final copolymer to get organosoluble and very low excimer-forming polymeric materials. Also a new route was provided in this study to prepare a series of polymeric materials with narrow distribution of fluorescence emission. The carbazole-containing materials had low excimer-forming sites, which might exhibit apparently good photoconductive properties and high carrier mobility in particular [26,27].

## 4. Conclusions

In conclusion, a new initiator (NBMBr) for ATRP was synthesized from the Diels–Alder reaction of cyclopentadiene and corresponding allyl bromide. The diblock copolymer, poly(CbzNB-*b*-NBMBr), was successfully prepared by living ROMP and used as a macroinitiator for ATRP. Strong carbazole fluorescence emissions were observed in the fluorescence spectra of poly(CbzNB-*b*-NBMBr), poly(HCbzNB-*b*-HNBMBr) and poly[(CbzNB-*b*-NBMBr)-*g*-PMMA]. This is the first ever attempt to prepare carbazole-containing multifunctional armed diblock polymeric materials, novel organosoluble fluorescent materials, by the combination of living ROMP and ATRP techniques. The methodology used here is expected to open up the possibility of producing entirely novel multi-functional armed fluorescent materials with new and potentially interesting properties, such as hole transport materials in molecular electronic devices.

## References

[1] Grubbs RH. Handbook of metathesis. Weinheim: Wiley; 2003.
[2] Feast WJ, Gilson VC, Johnson AF, Khosravi E, Mohsin MA. Polymer 1994;35:3542.
[3] Nomura E, Ito K, Kajiwara A, Kamachi M. Macromolecules 1997;30:2811.
[4] Liaw DJ, Chen TP, Huang CC. Macromolecules 2005;38:3533.
[5] Heroguez V, Gnanou Y, Fontanille M. Macromolecules 1996;30:4791.
[6] Heroguez V, Breunig S, Gnanou Y, Fontanille M. Macromolecules 1996;29:4459.
[7] Matyjaszewski K, Xia J. Chem Rev 2001;101:2921.
[8] Schorck RR. Acc Chem Res 1990;23:158.
[9] Grubbs RH, Tumas W. Science 1989;243:907.
[10] Kajiwara A, Matyjaszewski K. Macromolecules 1998;31:3489.
[11] Baumann R, Davis WM, Schrock RR. J Am Chem Soc 1997;119:3830.
[12] Webster OW, Hertler WR, Sogah DY, Farnham WB, Rajan-Babu TV. J Am Chem Soc 1983;105:5706.
[13] Liaw DJ, Tsai JS, Wu PL. Macromolecules 2000;33:6925.
[14] Bielawski CW, Morita T, Grubbs RH. Macromolecules 2000;33:678.
[15] Mecerreyes D, Dahan D, Lecomte P, Dubois P, Demonceau A, Noels AF, et al. J Polym Sci A Polym Chem 1999;37:2447.
[16] Liaw DJ, Liaw BY, Li U, Sillion B, Mercier R, Thiria R, et al. Chem Mater 1998;10:734.
[17] Kriegel RM, Rees WS, Weck M. Macromolecules 2004;37:6644.

[18] Matsuo A, Watanabe T, Hirao A. Macromolecules 2004;37:6283.

[19] Zhai G, Toh SC, Tan WL, Kang ET, Neoh KG, Huang CC, et al. Langmuir 2003;19:7030.

[20] Gratt J, Cohen RE. Macromolecules 1997;30:3137.

[21] Liaw DJ, Tsai CH. Polymer 2000;41:2773.

[22] Liaw DJ, Huang CC, Wu PL. Polymer 2001;42:9371.

[23] Beers KL, Gaynor SG, Matyjaszewski K. Macromolecules 1998;31:9413.

[24] Liaw DJ, Huang CC, Sang HC, Kang ET. Langmuir 1998;14:3195.

[25] Liaw DJ, Huang CC, Sang HC, Kang ET. Langmuir 1999;15:204.

[26] Strohriegl P, Grazulevicius JV. In: Nalwa HS, editor. Handbook of organic conductive molecules and polymer, vol. 1(11). New York, NY: Wiley; 1997. p. 553–620.

[27] Arora KS, Overberger CG. J Polym Sci, Polym Phys Ed 1986;24: 2275.