Synthesis and Characterization of a Novel Carbazole-containing Branched Random Copolymer Derived from \( \alpha \)-Norbornene Methylene Polystyrene Macromonomer via Ring-opening Metathesis Polymerization

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Abstract

A novel method for preparing \( \alpha \)-norbornene methylene polystyrene macromonomer (NBMPSt) is reported. NBMPSt macromonomer (\( M_n \) = \( 1.60 \times 10^5 \) and PDI = 1.26) had glass transition temperature (\( T_g \)) of 107 °C for polystyrene segment. Since the homopolymerization of NBMPSt macromonomer with number average molecular weight (\( M_n \)) \( 1.60 \times 10^5 \) could not be carried out by ring-opening metathesis polymerization (ROMP) with Ru catalyst \( [(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru=CHPh}, \text{Cy} = \text{cyclohexyl}] \), ring-opening metathesis copolymerization of NBMPSt macromonomer containing norbornene end group and norbornene monomer containing carbazole group (NBCbz) was investigated. A branched random copolymer containing carbazole groups and polystyrene segments, poly (NBMPSt-co-NBCbz), was successfully obtained (\( M_n \) = \( 3.99 \times 10^5 \) and PDI = 1.30). The molecular weight distributions of NBMPSt macromonomer and branched random poly(NBMPSt-co-NBCbz) are narrow. Branched random poly(NBMPSt-co-NBCbz) exhibited good solubility in a variety of solvents such as methylene chloride, chloroform, tetrahydrofuran, 1,2-dichlorobenzene, and even in xylene and benzene at room temperature or upon heating to 60 °C.

Key Words: ROMP, Ru Catalyst, Carbazole, Branched, Random Copolymer

1. Introduction

There have been a number of studies concerning the synthesis and application of macromonomers in the literature [1-3]. In the past, macromonomers were used mainly for the synthesis of branched copolymers by their copolymerization with conventional monomers [1-3]. There has also been increasing interest in homopolymerization of macromonomers, which leads to polymacromonomers [1-3]. They are regular multibranched macromolecules with an extremely high branch density along the backbone [1-3]. It has been difficult to synthesize polymacromonomers with a high degree of polymerization because of the inherently low concentration of polymerizable groups and the steric hindrance of side chains [1-3]. In addition, ring-opening metathesis polymerization (ROMP) and atom transfer radical polymerization (ATRP) techniques have been adopted to prepare well-defined polymers with narrow polydispersities and terminal functionalities [1-3].

Norbornene derivatives containing carbazole group have recently been polymerized using
classical olefin metathesis catalysts such as RuCl₃, and RuCl₂(PPh₃)₃ via ROMP [4]. In our previous works, 5-(N-carbazolyl methyl)bicyclo[2.2.1]hept-2-ene (NBCbz) was successfully synthesized and their polymers also were prepared via ROMP [5,6]. The incorporation of the carbazole group could enhance the thermal stability of the polymer and provide electro-optical properties of the polymers [4-6].

We will describe here the synthesis of α-norbornene methylene polystyrene macromonomer (NBMPSt) using norbornene methylene bromide (NBMBr) as a new alkyl halide initiator. After purification, the resulting macromonomer (NBMPSt) was subsequently reacted with carbazole-containing norbornene monomer (NBCbz) using Ru catalyst [(Cy₃P)₂Cl₂Ru=CHPh, Cy = cyclohexyl] by ring-opening metathesis polymerization. A novel branched random copolymer of poly(NBMPSt-co-NBCbz) was obtained.

![Ru catalyst](image)

2. Experimental

2.1 Material

Bis(tricyclohexylphosphine)-benzylidenerum dichloride [(Cy₃P)₂Cl₂Ru=CHPh, Cy = cyclohexyl] was purchased from Strem, U.S.A. Dicyclopentadiene was purchased from Merck, Germany. Styrene (Merck) was distilled under vacuum just before polymerization. The synthesis of norbornene methylene chloride (NBMCl) (bp = 54–56 °C/11 mmHg) and norbornene methylene bromide (NBMBr) (bp = 75–78 °C/13 mmHg) was accomplished via the Diels-Alder condensation of freshly cracked dicyclopentadiene and the corresponding allyl chloride and allyl bromide, respectively [5]. The catalysts, CuBr (98%, Acros) and 2,2'-bipyridine (Merck), were used as received without purification. Solvents were purified by standard procedures. Carbazole-containing norbornene monomer (NBCbz) was prepared via the reaction of NBMCl with potassium carbazole salt in N,N-dimethylformamide (DMF) [5]. The product (NBCbz) was obtained as a solid (mp = 74–76 °C) [5]. The structure of NBCbz was characterized by ¹H and ¹³C NMR analyses [5].

2.2 Polymerization

Simple alkyl halides were used for atom transfer free radical polymerization (ATRP) as initiators and copper(I) complexes as catalysts. They are inexpensive and readily available [2].

2.3 Synthesis of α-Norbornene Methylen Polystyrene Macromonomer (NBMPSt)

To an ampoule, Cu(I)Br (0.39 g, 2.5 mmole), 2,2'-bipyridine (1.07 g, 7.5 mmole), norbornene methylene bromide (NBMBr) (0.47 g, 2.5 mmole), styrene (75 mmole) and toluene (10 mL) were added (Scheme I). The heterogeneous mixture was placed under vacuum and then degassed via a freeze-pump-thaw cycle thrice. After being degassed, the ampoule was stirred at 130 °C for 12 hrs. The polymer was washed, precipitated from methanol and reprecipitated from tetrahydrofuran (THF) into methanol three times. A new macromonomer of α-norbornene methylene polystyrene (NBMPSt) was obtained (Mₙ = 1.60 × 10⁵ and Mₙ/Mₗ = 1.26 by GPC).

2.4 Synthesis of Random Poly(NBMPSt-co-NBCbz)

A catalyst solution was prepared by dissolving 1 mg of Ru catalyst [(Cy₃P)₂Cl₂Ru=CHPh, Cy = cyclohexyl] (1.22 × 10⁻³ mmole) in 1 mL of anhydrous methylene chloride under an argon-filled drybox. A mixture of the NBMPSt macromonomer (0.3 g) and NBCbz (0.3 g) was dissolved in 5 mL of methylene chloride and then degassed via a freeze-pump-thaw cycle thrice. After it was degassed completely, the catalyst solution was injected into the mixture by syringe. The polymerization was carried out at 30 °C for 2 hrs. A branched random copolymer [poly(NBMPSt-co-NBCbz)] was obtained and precipitated from methanol. The branched random copolymer [poly(NBMPSt-co-NBCbz)] was reprecipitated from THF into methanol three times. Mₙ = 3.99 × 10⁵ and Mₙ/Mₗ = 1.30 by GPC (Figure 1). The structure of branched random poly(NBMPSt-co-NBCbz) was characterized by ¹H NMR analysis (Figure 2).

2.5 Instruments

Glass transition temperature (T_g) was measured with a Du Pont 9000 differential scanning calorimeter at a heating rate of 10 °C·min⁻¹. Weight-average (M_w) and number-average (M_n) molecular weights were determined by gel permeation chromatography (GPC). Four Waters
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Figure 1. GPC elution profile of branched random poly-(NBMPSt-co-NBCbz) (Mn = 3.99 × 10^5 and PDI = 1.30) (Ultrastyragel) columns 300 × 7.7 mm (guard, 500, 10^2, 10^3, 10^4 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. Polystyrene was used as the standard. ^1H-NMR spectra were obtained on a JEOL EX-400 operating at 399.65 MHz for proton.

3. Results and Discussion

A novel initiator, NBMBr, for atom transfer radical polymerization (ATRP) was synthesized by Diels-Alder reaction as shown below.

Norbornene methylene bromide (NBMBr) containing norbornene and alkyl bromide groups is suitable as an initiator for ATRP. A new macromonomer, polystyrene containing norbornene group

Figure 2. 400 MHz ^1H NMR spectrum obtained in CDCl₃ at 25 °C for branched random poly(NBMPSt-co-NBCbz)
Cyclopentadiene + CH₂═CH(CH₂)Br

\[ \text{Diels - Alder reaction} \]

\[ 180^\circ C, \text{8 hrs} \]

\[ \text{NBMPBr} \]

end group (NBMPSt), was prepared by ATRP using NBMPBr as an initiator. The initiator and the polymer dissolved well in the solvent and did not precipitate, although the catalyst system was not homogeneous. The mixture was heterogeneous due to the catalysts, Cu₁(byd)₂ and Br⁻Cu II(byd)₂ being insoluble in toluene (Scheme I). The number average molecular weight (\( M_n \)) of the resulting macromonomer (NBMPSt) was \( 1.60 \times 10^5 \) (\( M_w/M_n = 1.28 \)). In the \(^1\text{H} \) NMR spectrum of NBMPSt, the protons of polystyrene segment (\(-\text{CH}_2\text{C}(\text{H})\text{C}_6\text{H}_5:\text{6.}2\text{~7.}1 \text{ppm}\)) in the spectrum provided confirmation of the copolymer structure. The resulting macromonomer (NBMPSt) was soluble in a variety of solvents such as methylene chloride, chloroform, tetrahydrofuran, benzene, toluene, xylene, and even 1,2-dichloro-benzene at room temperature.

Gnanou et al. [3,8] reported that poly(ethylene oxide) with norbornene end group (PEO macromonomer) having higher molecular weight (\( M_n = 1.10 \times 10^5 \)) could not be polymerized. In this study, no metathesis polymerization occurred for macromonomer (NBMPSt) with molecular weight of \( 1.60 \times 10^5 \) [Scheme II(A)], but the norbornene end group of NBMPSt can still react with Ru catalyst [(Cy₃P)₂Cl₂Ru=CHPh, Cy = cyclohexyl] to provide an active metal carbene for ring-opening metathesis polymerization (ROMP) of norbornene monomer (NBCbz) [Scheme II(B)]. The expected branched random copolymer containing carbazole group and polystyrene segments, poly(NBMPSt-co-NBCbz), was obtained [Scheme II(B)]. The resulting branched random poly (NBMPSt-co-NBCbz) exhibited good solubility in a variety of solvents such as methylene chloride, chloroform, tetrahydrofuran, 1,2-dichlorobenzene, and even in xylene and benzene at room temperature or upon heating to 60 °C.

The gel permeation chromatographic (GPC) trace of random poly(NBMPSt-co-NBCbz) is shown in Figure 1. The clear shift of molecular weight without any shoulder indicates clean formation of the branched random copolymer. After random copolymerization, the molecular weight distribution still remained narrow (\( M_w/M_n = 1.30 \)). The structure of copolymer was analyzed by \(^1\text{H} \) NMR spectroscopy. Figure 2 illustrates the 400 MHz \(^1\text{H} \) NMR spectrum of poly(NBMPSt-co-NBCbz). Integration of the aromatic carbazole group (7.0~8.1 ppm), cyclic polynorbornene main chain (0.8~3.7 ppm), and polystyrene segment (\(-\text{CH}_2\text{C}(\text{H})\text{C}_6\text{H}_5:\text{1.}4\text{~1.}6 \text{ppm}; \text{−CH}_2\text{C}(\text{H})\text{C}_6\text{H}_5:\text{1.}8\text{~2.}0, \text{3.}9\text{~4.}2 \text{ppm}; \text{and} −\text{CH}_2\text{C}(\text{H})\text{C}_6\text{H}_5:\text{6.}3\text{~7.}5 \text{ppm}\)) in the spectrum confirmed the branched random copolymer structure.

Thermal properties of NBMPSt macromonomer and branched random poly (NBMPSt-co-NBCbz) were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Poly(NBMPSt-co-NBCbz) showed a \( T_g \) of 105 °C for polystyrene and 165 °C for NBCbz segment. The DSC curve for poly(NBMPSt-co-NBCbz) shows two glass transition temperatures indicating that phase separation occurs in the branched random copolymer. Thermogravimetric analysis (TGA) was conducted in air atmosphere as shown in Figures 3(A) and 3(B). The macromonomer (NBMPSt) was fairly stable up to a temperature around or above 320 °C. The temperature at 10% mass loss (\( T_{d,10\%} \)) of NBMPSt, as shown in Figure 3(A), was found to be 370 °C in air atmosphere. The branched random copolymer containing carbazole group and polystyrene segments [random poly-(NBMPSt-co-NBCbz)] showed better thermal stability than NBMPSt macromonomer, and the 10% weight loss temperature of branched random poly(NBMPSt-co-NBCbz) occurred at 390 °C in air atmosphere [Figure 3(B)]. This indicated that branched random copolymer containing carbazole group and polystyrene segment [random poly (NBMPSt-co-NBCbz)] could enhance thermal stability, owing to the incorporation of the car-bazole group in the polymer chain [5].
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Scheme I. Synthesis of NBMPSt macromonomer

Scheme II. Synthesis of branched random poly(NBMPSt-co-NBCbz)

4. Conclusion

Macromonomer containing norbornene end group (NBMPSt) was obtained by atom transfer radical polymerization (ATRP) using norbornene methylene bromide (NBMBr) as a new initiator. Macromonomer containing norbornene end group (NBMPSt) (\(\bar{M}_n = 1.60 \times 10^5\)) showed a glass transition temperature \(T_g\) of 107 \(^\circ\)C for polystyrene segment. A novel method of preparing new branched random copolymeric materials via a combination of atom transfer radical polymerization (ATRP) and ring-opening metathesis polymerization (ROMP) has been reported. The successful preparation of branched random copolymer containing carbazole groups and polystyrene segments [poly(NBMPSt-co-NBCbz)] was discussed. A branched random poly(NBMPSt-co-NBCbz) with number average molecular weight of 3.99 \(\times\) \(10^5\) was obtained. The incorporation of carbazole group enhances thermal stability of poly(NBMPSt-co-NBCbz) \([T_{d,10\%} = 390 \, ^\circ\text{C}]\).
Figure 3. TGA curves for (A) macromonomer (NBMPSt) and (B) its branched random copolymer containing carbazole groups [random poly(NBMPSt-co-NBCbz)] measured under air. Temperature was raised at a rate of 10 °C·min⁻¹.

References


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