An Efficient Synthesis of Ring-Opening Metathesis Monomers and Polymers Containing Carbazole and Other Electron-Rich Moieties

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Abstract: An efficient synthesis of ring-opening metathesis monomers and polymers containing ionizable moieties such as *N*-carbazolyl, 2-dibenzofuranyl, 2-dibenzothiophenyl, and 4-anisyl functionalities has been developed, using cation radical Diels–Alder cycloaddition chemistry to generate the appropriate norbornene-type monomers.

Keywords: carbazoles; cation radical Diels–Alder reaction; cycloaddition; radical ions; ring-opening metathesis polymerization (ROMP); ruthenium

Introduction

Molecules which contain the bicyclo[2.2.1]hept-2-ene (norbornene) structural moiety are well known to be especially reactive toward ring-opening metathesis polymerization (ROMP).[1] Further, the presence of readily ionizable groups, and especially the carbazolyl group, in polymers is capable of imparting desirable photoconductivity and photorefractivity properties upon the polymer, leading to useful applications as materials in optoelectronic devices.[2] Although the Diels-Alder addition of appropriate dienophiles to 1,3-cyclopentadiene is an efficient method for generating some monomers of the norbornene type, such additions typically are not feasible for electron-rich dienophiles. In contrast, cation radical Diels–Alder reactions are ideally suited to electron-rich dienophiles and their cycloadditions to 1,3-cyclopentadiene,[3] and this efficient chemistry has now been used to generate and polymerize norbornene monomers containing carbazolyl and other electron rich functionalities.

Results and Discussion

This research group has been active in developing the synthetic potential of the cation radical Diels-Alder reaction for nearly two decades.[3] This reaction has been found to be uniquely appropriate for the Diels–Alder addition of readily ionizable dienophiles to conjugated dienes and especially to cyclic conjugated dienes such as 1,3-cyclopentadiene, using the shelf-stable and commercially available catalyst tris(4-bromophenyl)aminium hexachloroantimonate ($\mathbf{1}^{+\cdot}$). The ionizable dienophiles (**2**) which have been most commonly employed are typically those which have an electron-donor group (EDG) in conjugation with the dienophilic π bond. A few such EDG's which are directly relevant to the present research are illustrated in Scheme 1, but the range of such groups which promote effective participation in the cation radical Diels–Alder reaction is wide.

The mechanisms of these reactions are relatively well known (Scheme 2)[4–7] and have been shown to proceed via electron transfer from the electron-rich dienophile to the catalyst to yield the corresponding dienophile cation radical, followed by addition of the latter to the neutral diene and then subsequent neutralization of the adduct cation radical by electron transfer from the monomer. The cycloaddition stage itself consists of a two step process involving an intermediate distonic cation radical. The availability of an efficient and direct synthesis of norbornene-type monomers (**3**) having electron-donor functionality thus presents an attractive opportunity for the generation of polymers containing ionizable functionality via ring-opening metathesis polymerization.

The simple case (**2a**) in which the EDG is *p*-anisyl was investigated first. The adduct **3a** has previously been obtained in 75% yield as a 4:1 mixture of the *endo*- and *exo-trans*-diastereoisomers.[8] The purified *endo*-isomer, obtained by silica gel chromatography using a petroleum ether eluent, was used for the polymerization studies. Polymerization using the Grubbs catalyst [bis(tricyclohexylphosphine)benzylidine

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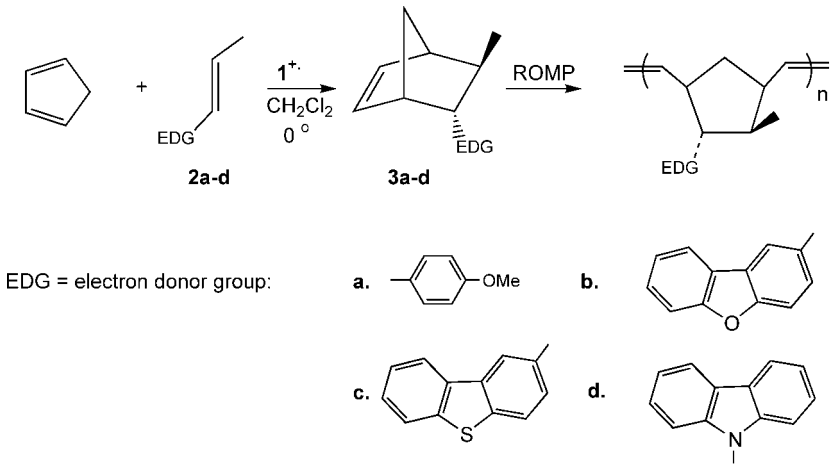
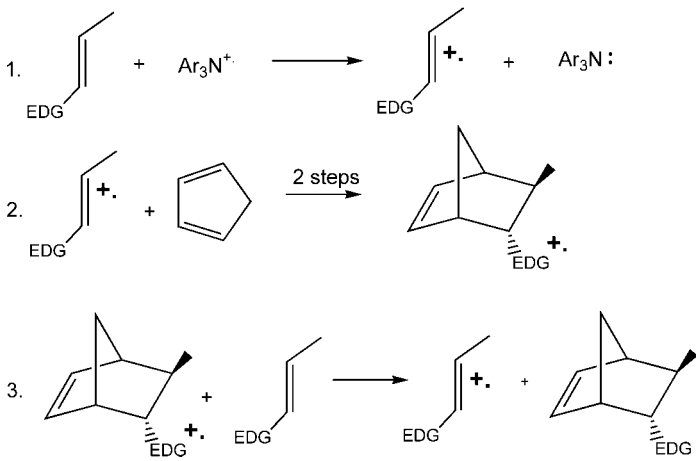


Scheme 1. Synthesis of norbornene-type monomers having electron-donating substituents via cation radical Diels–Alder cycloaddition and their ring opening metathesis polymerization to polymers having ionizable functionality; EDG = electron-donating group.



Scheme 2. The mechanism of the cation radical Diels–Alder cycloadditions.

ruthenium(IV) chloride] under standard dry-box conditions was efficient, leading to a ROMP polymer of M_W = 222,600 (PDI = 1.46). Integration of the four main chemical shift areas (aromatic : vinyl : MeO : aliphatic = 4 : 2 : 3 : 9) confirmed the gross structure of the polymer. Films of this polymer proved to be durable and transparent, and the polymer is thermally stable up to at least 400 °C.

A new monomer containing the 2-dibenzofuranyl group (**3b**) was then prepared by the cycloaddition of 2-(1-*trans*-propenyl)dibenzofuran (**2b**) to 1,3-cyclopentadiene. The adducts were obtained in 84% yield after a reaction time of only 3 minutes when using 15 mol % of the aminium salt catalyst (**1**$^{+\cdot}$). Polymerization of **3b** using the Grubbs catalyst generated a ROMP polymer of M_W = 87,500 (PDI = 1.57). A similar synthesis of **3c** via **2c** was then carried out. This monomer was converted in like manner to a ROMP polymer of M_W = 10,200 (PDI = 1.5).

Perhaps the most significant single goal of this research was to prepare structurally novel polymers containing the highly ionizable carbazole moiety. Recently, an improved synthetic procedure which uses a two-phase water/dichloromethane solvent system in conjunction with the commercially available tris(4-bromophenyl)aminium hexachloroantimonate (**1**$^{+\cdot}$) catalyst has been found to yield adducts of *N*-(*trans*-1-propenyl)carbazole (**2d**) with a wide variety of conjugated dienes in very good yields.[9] The Diels–Alder cycloaddition of this electron-rich dienophile to 1,3-cyclopentadiene proceeds cleanly in 72% yield (Scheme 1) to afford a 89 : 11 mixture of the diastereoisomeric *endo*- and *exo*-adducts **3d.** The polymerization of the *endo*-monomer using the Grubbs catalyst does in fact lead to a novel ROMP polymer having M_W = 26,600 (PDI = 1.60), which is currently being further investigated in relation to its photoconductivity and photorefractivity properties.

Conclusion

These results demonstrate the effectiveness of cation radical Diels–Alder cycloadditions for the synthesis of potential ROMP monomers having a variety of electron-donor substituents and ultimately for the generation of potentially useful polymers having readily ionizable groups. ROMP polymerization of the monomers with the Grubbs catalyst generates polymers of the expected gross structure, as confirmed by proton NMR spectra, and having a range of molecular weights up to ca. 220,000. The most promising result is the generation of ROMP polymers containing *N*-carbazolyl moieties. However, a range of electron-donor functionalities has been successfully installed, and the method appears to be quite general.

Experimental Section

General Remarks

Proton NMR spectra were recorded on a Bruker AC250 or a Varian UNITY INOVA 500 spectrometer. Chemical shifts (δ) are relative to tetramethylsilane, and coupling constants (*J*) are in Hz. Carbon NMR spectra were recorded on the Bruker 250 instrument. High resolution mass spectra (HR-MS) were recorded on a VGZAB-2E mass spectrometer. GC measurements were recorded using a Hewlett-Packard 6890 instrument with an HP 6890 Series Integrator. All chemicals used as starting materials were purchased from the Aldrich Company and used as received unless otherwise specified. The Grubbs catalyst was purchased from Strem Chemicals for Research. The dichloromethane solvent was dried by refluxing it over calcium hydride. The catalyst, tris(4-bromophenyl)aminium hexachloroantimonate, was synthesized according to a literature procedure.[10]

Synthesis of 2-(*trans*-1-Propenyl)dibenzofuran (2b)

This new electron rich dienophile was prepared by a three-step synthetic sequence involving propionylation of dibenzofuran, reduction of the ketone to the corresponding alcohol, and elimination to give the dienophile:

2-Propionyldibenzofuran
To a dry, three-neck, round-bottomed flask equipped with a magnetic stirrer, dibenzofuran (5 g, 0.003 mol) was added, followed by carbon disulfide (50 mL). After lowering the temperature of the reaction in an ice bath, 2.13 g (0.023 mol) of propionyl chloride was added, followed by the slow addition of $AlCl_3$ (3.68 g, 0.028 mol). After the addition was complete, the ice bath was removed, and the reaction mixture was stirred for an additional 17 h. The reaction mixture was carefully poured into a separating funnel containing crushed ice. Aqueous work-up, followed by chromatography on alumina (hexane : dichloromethane, 7 : 1 then 3 : 1) provided 3.46 g (52%) of 2-propionyldibenzofuran; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7.0 Hz, 3H), 3.08 (q, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.0 Hz, 1H), 7.57–7.53 (m, 2H), 7.95 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 8.54 (s, 1H); LR-MS, *m/z* = 225; HR-MS: calculated for $C_{15}H_{15}O_2$: 225.091555; found: 225.091410.

2-(1-Hydroxypropyl)dibenzofuran
The purified ketone from the previous reaction (3.46 g, 0.015 mol) was reduced with sodium borohydride (0.76 g, 0.020 mol) in ethanol (30 mL) for 4 h at room temperature. After quenching the reaction mixture with 10% aqueous acetic acid, followed by aqueous work-up, the pure alcohol product (3.60 g, 100%) was obtained; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.5 Hz, 3H), 1.92–1.78 (m, 2H), 2.17 (s, 1H), 4.73 (t, *J* = 6.6 Hz, 1H), 7.32–7.56 (m, 5H), 7.90 (s, 1H), 7.93 (s, 1H); LR-MS: *m/z* = 227; HR-MS: calculated for $C_{15}H_{15}O_2$: 227.107205; found: 227.107300.

2-(*trans*-1-Propenyl)dibenzofuran (2b)
To the proceeding alcohol (3.60 g, 0.016 mol) was added dry pyridine (10 mL), followed by the slow addition of $POCl_3$ (3.18 g, 0.021 mol) in an ice bath. After the reaction mixture was heated to refluxing for 12 h (120–130 °C), it was cooled to room temperature. Water (10 mL) was then added slowly, while the reaction mixture being cooled in an ice bath. After aqueous work-up and column chromatography on basic alumina (hexane : dichloromethane, 5 : 1), the pure product was obtained in 42% yield (1.4 g); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.92 (dd, J_1 = 6.6 Hz, J_2 = 1.5 Hz, 3H), 6.23–6.31 (m, 1H), 6.54 (d, *J* = 15.8 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.41–7.46 (m, 3H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.87 (s, 1H), 7.93 (d, *J* = 7.5 Hz, 1H); LR-MS, *m/z* = 209; HRMS: calculated for $C_{15}H_{13}O$: 209.096640; found: 209.097069.

Diels–Alder Cycloaddition of 2b to 1,3-Cyclopentadiene : Formation of *endo*-5-(2-Dibenzofuranyl)-(*trans*-6-methyl)-2-norbornene (3b)
To a solution of 200 mg (0.96 mmol) of 2-(*trans*-1-propenyl)-dibenzofuran and cyclopenta-1,3-diene (318 mg, 4.8 mmol) in 16 mL of anhydrous dichloromethane were added 118 mg (0.144 mmol) of the catalyst, tris(4-bromophenyl)aminium hexachloroantimonate ($\mathbf{1}^+$), dissolved in 10 mL of anhydrous dichloromethane. The reaction was quenched after 3 minutes by adding saturated potassium carbonate-methanol solution. Aqueous work-up and column chromatography on basic alumina (hexane : dichloromethane, 15 : 1), afforded a total of 220 mg (84% yield) of the diastereoisomeric *trans*-Diels-Alder adducts having an *endo : exo* ratio of 5 : 1; ^{1}H NMR (250 MHz, $CDCl_3$): = δ 1.27 (d, *J* = 6.9 Hz, 3H, methyl), 1.54 (m, 1H, H7-*anti*), 1.79 (m, 1H, H6), 1.92 (m 1H, H7-*syn*), 2.56 (s, 1H, H1), 2.92 (d, *J* = 4.5 Hz, 1H, H5), 3.06 (s, 1H, H4), 5.91 (dd, *J* = 5.7 Hz, *J* = 2.8 Hz, 1H, H2), 6.39 (dd, J_1 = 5.7 Hz, J_2 =3.1 Hz, 1H, H1), 6.90 (d, *J* = 6.8 Hz, 1H), 7.26–7.45 (m, 3H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.71 (s, 1H), 7.92 (d, *J* = 7.6 Hz, 1H); LRMS: *m/z* = 275; HR-MS: calculated for $C_{20}H_{19}O$: 275.143590; found: 275.143263.

Synthesis of 2-(*trans*-1-Propenyl)dibenzothiophene

2-Bromodibenzothiophene
To a solution of dibenzothiophene (5 g, 0.027 mol) in carbon disulfide (15 mL) was added bromine (4.13 g, 0.027 mol) over a period of 20 minutes in an ice bath. The mixture was stirred at room temperature for 2.5 h under nitrogen, fil-

tered and washed with ethanol. The filtered product was subjected to column chromatography on silica gel (hexane : dichloromethane, 6 : 1), and the pure product was obtained; Yield: 1.02 g (14.4%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.50 (m, 2H), 7.53 (dd, J_1 = 8.7, J_2 = 1.8 Hz, 1H), 7.69 (d, J = 8.7 Hz, 1H), 7.83 (m, 1H), 8.09 (m, 1H), 8.26 (d, J = 1.8 Hz, 1H); LR-MS: m/z = 265; HR-MS: calculated for $C_{12}H_7SBr$: 261.945183; found: 261.945002.

2-(1-Hydroxypropyl)dibenzothiophene
2-Lithiodibenzothiophene was prepared by treating a suspension of 2-bromodibenzothiophene (1.0 g, 3.8 mmol) in dry ether (30 mL) with *n*-butyllithium (1.6 M solution in *n*-hexane, 3.6 mL, 5.7 mmol) under a dry atmosphere of nitrogen for 5 minutes at 0 °C. To the resulting mixture, propionaldehyde (0.265 g, 4.6 mmol) was added dropwise, and the reaction mixture was stirred at 0 °C for 30 minutes. Water was added and the solution was extracted with dichloromethane. Removal of the solvent followed by column chromatography on alumina (hexane : dichloromethane, 7 : 1, then acetone) yielded 750 mg (81.6%) of 2-(1-hydroxypropyl)dibenzothiophene; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (t, J = 7.3 Hz, 3H), 1.81–1.94 (m, 2H), 4.77 (t, J = 6.6 Hz, 1H), 7.41–7.45 (m, 3H), 7.79–7.85 (m, 2H), 8.13–8.17 (m, 2H); LR-MS: m/z = 243; HR-MS: calculated for $C_{15}H_{15}OS$: 243.084362; found: 243.084362.

2-(*trans*-1-Propenyl)dibenzothiophene (2c)
To the preceeding alcohol (750 mg, 3.1 mmol) was added dry pyridine (5 mL), followed by the slow addition of $POCl_3$ (713 mg, 4.6 mmol) in an ice bath. After the reaction mixture was heated to refluxing for 5.5 h (120–130 °C), it was cooled to room temperature. Water was then added slowly, while the reaction mixture being cooled in an ice bath. After aqueous work-up and column chromatography on silica gel (hexane), the pure product was obtained in 12% yield (83 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.95 (dd, J_1 = 6.6 Hz, J_2 = 1.5 Hz, 3H), 6.29–6.41 (m, 1H), 6.57 (dd, J_1 = 15.9 Hz, J_2 = 1.8 Hz, 1H), 7.41–7.48 (m, 3H), 7.75 (d, J = 8.4 Hz, 1H), 7.81–7.85 (m, 1H), 8.06 (d, J = 1.5 Hz, 1H), 8.11–8.17 (m, 1H); LR-MS: m/z = 225; HR-MS: calculated for $C_{15}H_{13}S$: 225.073797; found: 225.073899.

***endo*-5-(2-Dibenzothiophenyl)-*trans*-6-methyl-2-norbornene (3c)**
To a solution of 82 mg (0.366 mmol) of 2-(*trans*-1-propenyl)-dibenzothiophene and cyclopenta-1,3-diene (121 mg, 1.83 mmol) in 11 mL of anhydrous dichloromethane were added 45 mg (0.055 mmol) of the catalyst, tris(4-bromophenyl)aminium hexachloroantimonate, dissolved in 5 mL of anhydrous dichloromethane. The reaction was quenched after 12 minutes by adding saturated potassium carbonate-methanol solution. Aqueous work-up and column chromatography on basic alumina (hexane : dichloromethane, 10 : 1), yielded a total of 92 mg (86.8% yield) of the diastereoisomeric *trans*-Diels–Alder adducts; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.30 (dd, J_1 = 6.9 Hz, J_2 = 1.2 Hz, 3H, methyl), 1.56 (m, 1H, H7-*anti*), 1.79 (d, J = 8.4 Hz, 1H, H6), 1.88 (m 1H, H7-*syn*), 2.59 (s, 1H, H1), 2.95 (t, J = 3.9 Hz, 1H, H5), 3.09 (s, 1H, H4), 5.94 (dd, J = 5.4 Hz, J = 2.7 Hz, 1H, H2), 6.42 (dd, J_1 = 8.4 Hz, J_2 = 3.6 Hz, 1H, H3), 7.29–7.46 (m, 3H), 7.70 (d, J = 8.1 Hz, 1H), 7.81–7.84 (m, 1H), 7.95 (s, 1H), 8.12–8.15 (m, 1H); LR-MS: m/z = 291; HR-MS: calculated for $C_{20}H_{19}S$: 291.120748; found: 291.120559.

General Polymerization Procedure
All handling of the catalyst and polymerization was done in a nitrogen-filled dry-box. Dichloromethane employed as a polymerization solvent was dried by distillation over CaH_2 and degassed under vacuum by freezing it in liquid nitrogen. Solutions of the Grubbs catalyst, $RuCl_2(=CHPh)(PCy_3)_2$,were freshly prepared for each reaction by adding 1.0 mL of dichloromethane to 15 mg of catalyst in a serum-capped flask. The catalyst solution was transferred by syringe to a solution of 190 mg of **3** in 4.0 mL of CH_2Cl_2. The light pink solution was then stirred inside the dry-box for 2.5 h at room temperature. The reaction was terminated by the addition of two drops of butyl vinyl ether, and the color of the solution changed from pink to yellow. After termination, the solution was stirred for an additional 5 minutes, taken out of the dry-box, and the mixture poured into methanol (50 mL) to precipitate the polymer. After drying under vacuum, the polymers were obtained as fluffy white solids. The pure *endo*-isomers used in the polymerization were obtained by silica gel chromatographic separation of the *endo*-rich mixture by elution with petroleum ether.

Polymerization of 3a
The polymer obtained from 168 mg of **3a** was isolated as a white solid (130 mg, 77.4%) having M_W = 222,600 (PDI = 1.46); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.8–3.2 (9H, aliphatic), 3.6–3.8 (3H, methoxy), 4.5–5.5 (2H, olefinic), 6.5–7.2 (4H, aromatic).

Polymerization of 3b
The polymer obtained from 190 mg of **3b** was isolated in 63% yield (120 mg) as a fluffy white solid having M_W = 87,500 (PDI = 1.57); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.7–3.4 (9H, aliphatic), 4.3–5.7 (2H, olefinic), 6.8–7.9 (7H, aromatic); T_d (onset) 409.2 °C under nitrogen; no T_g prior to thermal decomposition under nitrogen.

Polymerization of 3c
The polymer obtained from 92 mg of **3c** was isolated in 77% yield (71 mg) as a fluffy white solid having M_W = 10,200 (PDI = 1.52); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.7–3.1 (9H, aliphatic), 4.9–5.7 (2H, olefinic), 6.8–8.1 (7H, aromatic); T_d 151.6 °C under nitrogen; no glass transition temperature (T_g) prior to thermal decomposition under nitrogen.

Polymerization of 3d
The polymer obtained from 133 mg of **3d** was isolated in 75% yield (100 mg) as a fluffy white solid having M_W = 26,600 (PDI = 1.60); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.7–3.7 (8H, aliphatic), 4.0–5.8 (3H, olefinic and alpha to nitrogen), 6.8–7.9 (7H, aromatic); T_d (onset) 409.2 °C under nitrogen; no T_g prior to thermal decomposition under nitrogen.

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