

Block and Random Living, Ring-Opening Metathesis Copolymerization of Functionally Differentiated Carbazole-Containing Norbornene Monomers

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Abstract: The synthesis of novel diblock polymers containing both a potential charge transport and a non-linear optic block has been accomplished. The synthesis exploits the living, ring-opening metathesis block copolymerization of two norbornene type monomers, one of which contains an unsubstituted *N*-carbazolyl ring while the other has a bromo substituent at the 3-position of the carbazole ring. Conversion of the bromo functionality to a 2,2-dicyanovinyl group introduces the non-linear optic property. The first monomer was prepared by the previously reported efficient cation radical Diels–

Alder cycloaddition of *N-trans*-1-propenylcarbazole to 1,3-cyclopentadiene, while the second was obtained by *N*-bromosuccinimide bromination of the first monomer. For purposes of comparison, the corresponding random copolymer was also synthesized.

Keywords: block polymerization; carbazoles; polymers; cation radical Diels–Alder reaction; charge transport; living polymerization; non-linear optic; photorefractive effect; ring-opening metathesis polymerization (ROMP); ruthenium.

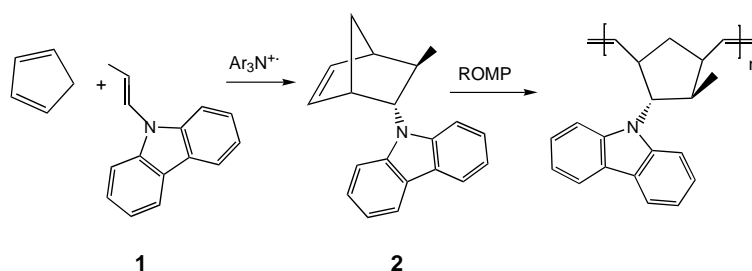
Introduction

Cation radical cycloaddition chemistry has recently been found in this laboratory to have useful applications to polymer synthesis via two distinctly different strategies. First, cation radical chain cycloaddition polymerization of difunctional, electron-rich alkene monomers has recently been found to represent a fundamentally new mechanism for polymerization.^[1] These polymerizations involve the generation of monomer cation radicals via initiation with sub-stoichiometric amounts of the readily available and shelf-stable cation radical salt tris(4-bromophenyl)aminium hexachloroantimonate, followed by the cycloaddition of monomer cation radicals to neutral monomer to give a cyclodimer (either cyclobutane or Diels–Alder) cation radical. Intramolecular hole transfer from the cycloaddition site to the second alkene functionality of the dimer cation radical then yields a reactive alkene dimer cation radical which can add to another molecule of neutral monomer, thereby yielding a trimer cation radical, et cetera. Alternating cycloaddition and intramolecular hole transfer steps then are repeated in the propagation cycle, leading to cycloaddition polymers of novel structure and having molecular weights up to 100,000. Application of this new polymerization concept to 3,6-bis(*trans*-1-propenyl)carbazole is especially efficient.^[2] Still more recently, it has been shown that cation radical

Diels–Alder cycloadditions of highly electron-rich, monofunctional monomers such as *N*-(*trans*-1-propenyl)carbazole to 1,3-cyclopentadiene give high yields of norbornene adducts which prove to be effective monomers for the synthesis of novel carbazole-containing polymers *via* ring-opening metathesis polymerization (ROMP).^[3] We now report the synthesis of an analogous norbornene monomer which has a bromine substituent at the 3-position of the carbazole ring, and the subsequent diblock and random living ROMP copolymerizations of the brominated and unbrominated norbornene monomers. The provision of the bromine functionality at the 3-position of the carbazole moiety then facilitates the conversion of these carbazole moieties to non-linear optic (NLO) functionalities containing the dicyanovinyl moiety, resulting in the formation of novel block and random copolymers which have both charge transport (CT) and non-linear optic (NLO) moieties essential for photorefractive materials.^[4]

Results and Discussion

Polyvinylcarbazole (PVK) and related polymers containing carbazole moieties are especially important charge transport polymers for organic light-emitting diodes (OLED's) and as photorefractive (PR) materials for electrooptic devices.^[4] The convenient availability of



Scheme 1.

two new structural types of carbazole polymers, as mentioned above, ignites interest in the possibility of developing these new polymers as useful materials. Of special interest in connection with the present research is the possibility of forming novel photorefractive (PR) polymers which contain two of the three [CT, NLO, and CG (charge generating)] moieties essential for the photorefractive effect in discrete blocks within the same polymeric material. Block copolymers were considered preferable to random copolymers in that interspersing the less readily ionizable NLO functionalities with the CT moieties appeared likely to have a deleterious effect upon the efficiency of charge transport along a polymer chain. The incorporation of both CT and NLO functionalities into the same polymer chain was intended to maximize the PR effect by minimizing waste space possibly associated with the use of distinct CT and NLO molecules and maximizing the interaction of the NLO moieties with the electric field generated by charge transport. The ready availability of carbazole-containing monomers of the norbornene type was seen as providing potential access to efficient ring-opening metathesis polymerization (ROMP), a living polymerization method which is especially amenable to block copolymerization.^[5]

The synthesis and ring-opening metathesis polymerization (ROMP) of the *endo*-Diels-Alder adduct (**2**) of *N*-(*trans*-1-propenyl)carbazole (**1**) with 1,3-cyclopentadiene has previously been reported (Scheme 1).^[3] Since it was critical to the proposed synthesis of a diblock polymer that this polymerization be a living polymerization, the polymerization of **2** has now been re-investigated at three different monomer:catalyst ratios using bis(tricyclohexylphosphine)(benzylidene)ruthenium dichloride as the catalyst. Living polymerization was confirmed by the observed linear relationship between M_w and the monomer:catalyst ratio (Table 1). Further, the low polydispersities are also consistent with a living polymerization. This polymerization was also investigated for different reaction times at a monomer:catalyst ratio of 50:1 (Table 2). Molecular weights were unchanged after 1 h.

As a convenient comonomer for the proposed synthesis, the 3-bromo derivative (**3**) of **2** was selected. This monomer proved to be conveniently available from **2** via

Table 1. Weight average molecular weights (M_w) and polydispersity indices (PDI) in the polymerization of monomers **2** and **3** at various $[M]/[I]$ (monomer/catalyst) molar ratios using $\text{RuCl}_2(=\text{CHPh})(\text{Pcy}_3)_2$ as the catalyst at room temperature ($[M] = 0.05 \text{ M}$; solvent: dichloromethane). Results determined by GPC using polystyrene calibration standards.

$[M]/[I]$	M_w [g mol^{-1}]	PDI
100 ^[a]	48,000	1.42
50 ^[a]	20,500	1.25
33 ^[a]	14,400	1.25
100 ^[b]	62,500	1.35

^[a] Monomer **2**. Reaction time of 1 h.

^[b] Monomer **3**. Reaction time of 1.5 h.

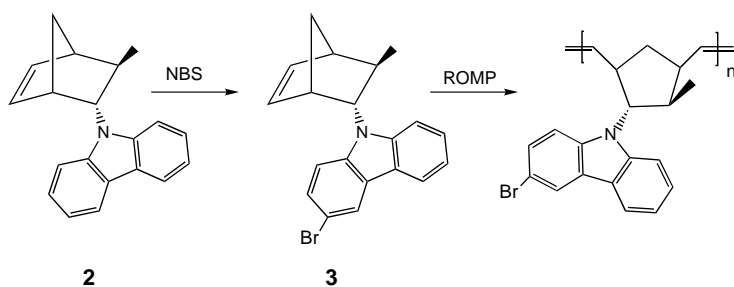
Table 2. Weight average molecular weights (M_w) and polydispersity indices (PDI) in the polymerization of monomer **2** at different reaction times, using $[M]/[I] = 50:1$.

Reaction Time [h]	M_w [g mol^{-1}]	PDI
1	24,600	1.32
1.25	25,300	1.24
1.5	25,300	1.24

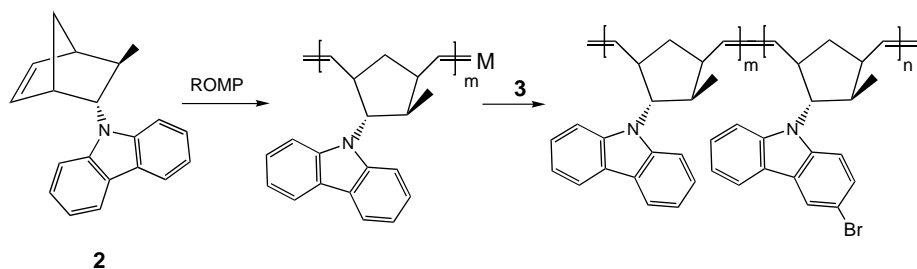
N-bromosuccinimide bromination (Scheme 2), and the bromo functionality permits efficient subsequent installation of the desired 2,2-dicyanovinyl NLO functionality. The ROMP polymerization of **3** was carried out, affording a polymer of M_w 62,500 and PDI 1.35 (Table 1).

The block copolymerization of **2** and **3** was then performed, using **2** as the first monomer and a **2:3** ratio of 2:1, with the aim of obtaining a block copolymer having approximately 33% NLO moieties (Scheme 3).^[5] The block copolymer, having M_w 36,400 and PDI 1.5, was isolated in 93% yield, corresponding to the efficient consumption of both monomers (Table 3). For comparison purposes, to evaluate the effectiveness of having separate blocks of CT and NLO moieties, the corresponding random copolymer was prepared by subjecting a 2:1 mixture of **2** and **3** to identical ROMP polymerization conditions.

The efficiency of the conversion of the bromo functionality to the desired NLO functionality was first



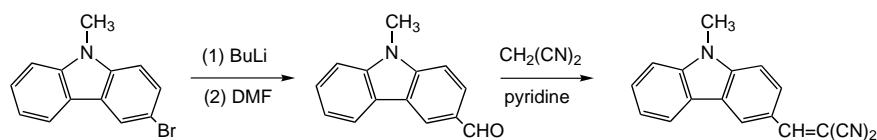
Scheme 2.



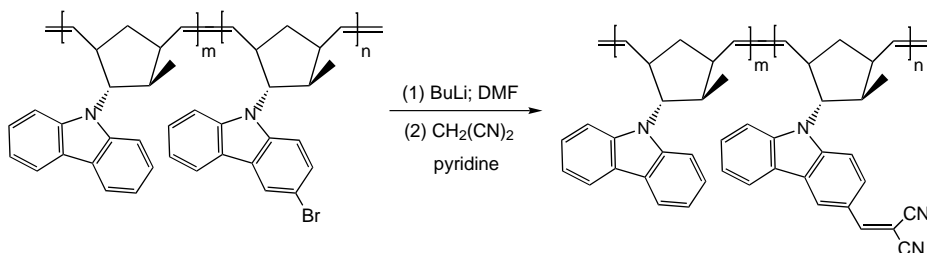
Scheme 3.

Table 3. Weight average molecular weights and polydispersity indices of the brominated block polymer, the corresponding formylated block polymer, and the dicanovinylated block polymer for 50:1 monomer: catalyst ratios.

Polymer	Yield [%]	M_w [g mol ⁻¹]	PDI
Block copolymer	93	36,400	1.5
Formylated block copolymer	88	46,100	1.71
Cyanovinylated block copolymer	81	42,000	3.01



Scheme 4.



Scheme 5.

explored *via* a model compound, 3-bromo-*N*-methylcarbazole (Scheme 4). Treatment of the latter with butyllithium, followed by reaction of the lithio compound with DMF provided the desired aldehyde in 77% yield. The reaction of the latter with malononitrile gave the pure 2,2-dicyanovinyl compound in 60% yield.

The same reactions were then carried out upon both the diblock and random copolymers (Scheme 5). The yields, weight average molecular weights and polydispersities of the block copolymers having bromo, formyl, and dicyanovinyl functionalities are shown in Table 3 and those of the corresponding random copolymers in

Table 4. The physical properties of the block and random copolymers are compared in Table 5. The increase in the PDI which occurs upon cyanovinylolation of the block, but not the random, copolymer is somewhat surprising. This could possibly indicate that block polymerization is not proceeding exclusively, but that some homopolymer of the brominated monomer is formed along with the predominant block copolymer. Degradation of the polymer during dicyanovinylolation appears highly unlikely since an analogous increase in PDI is not obtained in the case of the random polymer, and the model dicyanovinylolation proceeds without problems.

The presence of the formyl and dicyanovinyl groups is clearly revealed by ^1H and ^{13}C NMR, UV, and IR spectroscopy. On the basis of the model reactions, it is estimated that the efficiency of installation of NLO functionalities in the polymers is approximately 45%. Superimposed GPC traces of the three diblock polymers (containing bromo, formyl, and dicyanovinyl functionalities) are illustrated in Figure 1. All of the polymers appear to be stable thermally, as illustrated by the representative TGA trace for the diblock CT/NLO polymer (Figure 2) and the T_d 's listed in Table 5. The long wave length visible absorption of the NLO functionalities in both the block and random copolymers is at 415 nm.

The photoconductivities and photorefractivities of these novel polymers are currently being investigated in collaboration with Professors George Malliaras (Cornell) and W. E. Moerner (Stanford), respectively.

Conclusions

Diblock and random copolymers containing carbazole moieties as a potential charge transport block and 3-

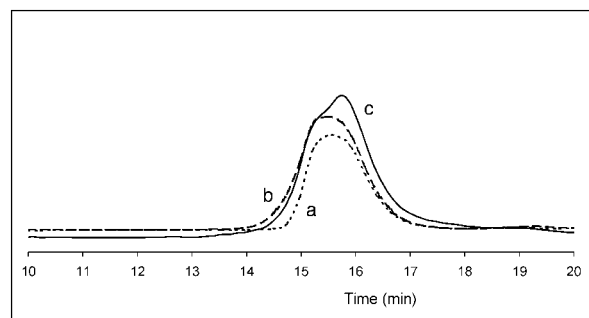


Figure 1. TGA curves for the unsubstituted homopolymer (a), block copolymer (b) and random copolymer (c) measured under nitrogen. Temperature was raised at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

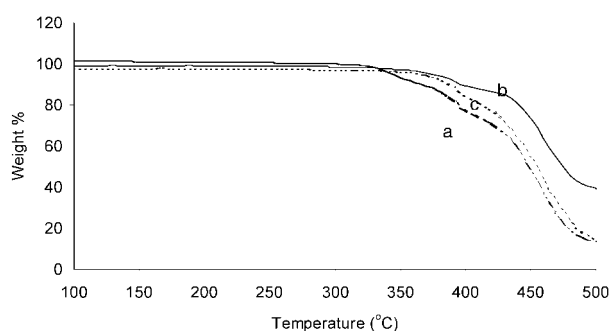


Figure 2. GPC elution profiles (taken in THF at room temperature at a flow rate of 1.0 mL min^{-1}): (a) block copolymer; (b) formylated block copolymer; (c) cyanovinylated block copolymer.

(2,2-dicyanovinyl)carbazole moieties as a potential non-linear optic block have been synthesized by living, ring-opening metathesis polymerization of appropriate norbornene monomers. The norbornene monomer appropriate for a charge transport block was efficiently

Table 4. Weight average molecular weights and polydispersity indices for the random, brominated copolymer and the corresponding formylated and dicyanovinylated copolymers.

Polymer	Yield [%]	M_w [g mol^{-1}]	PDI
Random copolymer	98	31,600	1.35
Formylated random copolymer	80	43,700	1.57
Dicyanovinylated random copolymer	68	44,100	1.62

Table 5. A summary of the weight average molecular weights (M_w), polydispersity indices (PDI), glass transition temperatures (T_g) and thermal decomposition temperatures (T_d) of the dicyanovinylated block and random copolymers.

Polymer	Yield [%]	$M_w^{[a]}$ [g mol^{-1}]	PDI ^[a]	$T_g^{[b]}$ [$^{\circ}\text{C}$]	$T_{d\ 2\%}^{[c]}$ [$^{\circ}\text{C}$]
Block copolymer	81	42,000	3.01	242	368
Random copolymer	68	44,100	1.62	238	374

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

^[b] DSC measurements were conducted at a heating rate of $15\text{ }^{\circ}\text{C min}^{-1}$.

^[c] Temperature at which 2% weight loss was determined by TGA in nitrogen at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

prepared by means of the cation radical Diels–Alder addition of *N*-(*trans*-1-propenyl)carbazole to 1,3-cyclopentadiene. The second monomer was prepared by *N*-bromosuccinimide monobromination of the first monomer at the 3-position of the carbazole ring. Subsequent to ring-opening metathesis copolymerization of these two monomers, the bromine functionalities were converted to 2,2-dicyanovinyl groups via the corresponding aldehyde. The polymers have MW's of about 40,000 and are thermally quite stable although they have rather high Tg's.

Experimental Section

General Remarks

Proton and carbon NMR spectra were recorded on a Varian UNITY PLUS 300 or a Varian UNITY INOVA 500 spectrometer. Chemical shifts (δ) are relative to tetramethylsilane, and coupling constants (J) are in Hz. Carbon spectra were recorded on the Bruker 250 instrument. High resolution mass spectra (HRMS) were recorded on a VGZAB-2E mass spectrometer. GC measurements were recorded using a Hewlett-Packard 6890 instrument with an HP 6890 Series Integrator. Gel permeation chromatography (GPC) was carried out in tetrahydrofuran using a Waters 510 HPLC pump, Waters 401 differential refractometer, with two PLGel 10 μ MIXED-B columns. The GPC analyses were calibrated with polystyrene standards. Thermal analyses were performed with a Perkin-Elmer DSC-7 Differential Scanning Calorimeter and a Perkin-Elmer TGA-7 Thermogravimetric Analyzer under a nitrogen atmosphere. 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.^[6]

3-Bromocarbazole

To a suspension of 3.48 g carbazole (0.02 mol) in 30 mL of dry acetonitrile were slowly added 3.60 g of *N*-bromosuccinimide (NBS; 0.02 mol). The reaction mixture was stirred for 21 h at room temperature under nitrogen, and filtered. The solid was washed with cold acetonitrile, and dried in vacuum. The product was recrystallized from EtOH, and a off white solid was obtained; yield: 4.4 g (45%); ¹H NMR (300 MHz, CDCl₃): δ = 7.25 (m, 3H), 7.42 (m, 2H), 7.48 (dd, J_1 = 8.7 Hz, J_2 = 1.8 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 8.17 (s, 1H); LRMS (CI): m/z = 246 (M + 1); HRMS (CI): m/z = 245.991704 (calcd. for C₁₂H₉N₁Br₁: 245.991835).

3-Bromo-9-methylcarbazole

To a solution of 3.15 g of 3-bromocarbazole (0.013 mol) in 15 mL of dry *N,N*-dimethylformamide were slowly added 1.95 g of K₂CO₃ (0.014 mol) and, after stirring for 30 minutes at

room temperature, a mixture of 2.0 g methyl iodide (0.014 mol) and 3 mL dry DMF was added dropwise. After 1 h of additional stirring at room temperature, the solution was refluxed for 19 h. The mixture was diluted with water and extracted three times with ethyl acetate. Combining the extracts, washing, drying and evaporating the solvents afforded 3-bromo-9-methylcarbazole. The product was purified by column chromatography on silica gel (petroleum ether); yield: 2.23 g (68.6%); ¹H NMR (300 MHz, CDCl₃): δ = 3.81 (s, 3H), 7.24 (m, 2H), 7.38 (d, J = 8.1 Hz, 1H), 7.48 (d, J = 7.8 Hz, 1H), 7.53 (dd, J_1 = 8.7 Hz, J_2 = 1.8 Hz, 1H), 8.02 (d, J = 7.2 Hz, 1H), 8.18 (s, 1H); ¹³C NMR (300 MHz, CDCl₃): δ = 28.7, 108.5, 109.6, 111.4, 119.0, 120.2, 121.4, 122.7, 124.1, 126.2, 128.0, 139.2, 141.0; LRMS (CI): m/z = 260 (M).

3-Formyl-9-methylcarbazole

A solution of 504 mg (1.94 mmol) of 3-bromo-9-methylcarbazole dissolved in a mixture of 30 mL of dry ether and 10 mL of dry benzene was kept at room temperature while 2.4 mL of *n*-butyllithium (3.88 mmol) was added, with stirring, over a 10 minute period. After 3 h at this temperature, 0.3 mL of *N,N*-dimethylformamide (3.88 mmol) was slowly added and the mixture stirred further at 30 °C for 5 h. The reaction mixture was carefully quenched by the addition of saturated NH₄Cl at 0 °C, until the solution became acidic. After extraction with dichloromethane, the solution was washed successively with water, with saturated NaHCO₃ and with saturated NaCl solution. After drying over anhydrous Na₂SO₄, the solvent was evaporated to provide the corresponding aldehyde. The product was further purified by column chromatography on silica gel (petroleum ether:dichloromethane, 3:1 then dichloromethane:methanol, 18:1); yield: 312 mg (77%). The corresponding reaction in benzene as solvent gave only a 47.1% yield: ¹H NMR (300 MHz, CDCl₃): δ = 3.85 (s, 3H), 7.31 (ca. t, J = 7.5 Hz, 1H), 7.42 (d, J = 8.1 Hz, 2H), 7.53 (ca. t, J = 8.2 Hz, 1H), 7.99 (dd, J_1 = 8.4 Hz, J_2 = 1.5 Hz, 1H), 8.12 (d, J = 7.8 Hz, 1H), 8.56 (s, 1H), 10.05 (s, 1H); LRMS (CI): m/z = 210 (M + 1); HRMS (CI): m/z = 210.090962 (calcd. for C₁₄H₁₂N₁O₁: 210.091889).

N-Methyl-3-(2,2-dicyanovinyl)carbazole

A mixture of malononitrile (82.7 mg, 1.25 mmol) and dry pyridine (108 mg, 1.37 mmol) in 5 mL of dry benzene was stirred at ambient temperature for 30 minutes under nitrogen, followed by the addition of a solution of 3-formyl-9-methylcarbazole (238 mg, 1.14 mmol) in 10 mL of dry benzene. The reaction mixture was heated under reflux for 21.5 h and cooled to room temperature followed by washing with water, drying with sodium sulfate and evaporating. The product was purified by column chromatography on silica gel (hexane:dichloromethane, 2:1 then 1:1); yield: 227 mg (60%); ¹H NMR (300 MHz, CDCl₃): δ = 3.90 (s, 3H), 7.35 (ca. t, J = 7.8 Hz, 1H), 7.45 (d, J = 9.0 Hz, 2H), 7.57 (ca. t, J = 7.8 Hz, 1H), 7.83 (s, 1H), 8.09 (m, 2H), 8.61 (s, 1H); IR (KBr pellet,): ν = 1598 ($\nu_{C=C}$, aromatic), 1635 ($\nu_{C=C}$, alkene), 2221 cm⁻¹ ($\nu_{C\equiv N}$, nitrile); UV (dichloromethane): λ_{max} = 291, 326, 410 nm; LRMS (CI): m/z = 258 (M + 1); HRMS (CI): m/z = 258.103195 (calcd. for C₁₇H₁₂N₃: 258.103123).

***endo*-5-[9-(3'-Bromocarbazolyl)]-*trans*-6-methyl-2-norbornene**

To a solution of 452 mg of NBS (2.54 mol) in 56 mL of dry dichloromethane was slowly added a solution of 630 mg of *endo*-5-(9-carbazolyl)-*trans*-6-methyl-2-norbornene^[7] (2.31 mmol) in 20 mL of dry dichloromethane. The reaction mixture was stirred for 2 h at room temperature under nitrogen, and evaporated. The resulting residue was dissolved in dichloromethane, washed with water and dried in anhydrous Na₂SO₄. The product was purified by column chromatography on silica gel (petroleum ether); yield: 460 mg (56.6%); ¹H NMR (300 MHz, CDCl₃): δ = 1.27 (d, *J* = 6.6 Hz, 3H), 1.62 (d, *J* = 9.0 Hz, 1H, H7-*anti*), 1.90 (d, *J* = 9.0 Hz, 1H, H7-*syn*), 2.77 (s, 1H, H1), 2.90 (m, 1H, H6), 3.24 (s, 1H, H4), 4.67 (t, *J* = 3.8 Hz, 1H, H5), 6.00 (m, 1H, H3), 6.68 (m, 1H, H2), 7.22 (m, 2H), 7.41 (m, 2H), 7.55 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 7.2 Hz, 1H), 8.16 (s, 1H); ¹³C NMR (300 MHz, CDCl₃): δ = 20.8, 34.5, 45.7, 49.1, 49.5, 66.8, 111.4, 111.8, 113.6, 119.1, 120.0, 122.3, 122.5, 125.3, 125.9, 127.7, 134.8, 139.5, 141.4; LRMS (CI): *m/z* = 352 (M); HRMS (CI): *m/z* = 352.070905 (calcd. for C₂₀H₁₉N₁Br₁: 352.070086)

Ring-Opening Metathesis Polymerization of *endo*-5-(9-Carbazolyl)-*trans*-6-methyl-2-norbornene

In various runs, the reaction time and monomer to initiator ratio were varied independently to determine the proper reaction conditions.

Ring-Opening Metathesis Polymerization of *endo*-5-[9-(3'-Bromocarbazolyl)]-*trans*-6-methyl-2-norbornene

The ring-opening metathesis polymerization was carried out using the metathesis catalyst, bis(tricyclohexylphosphine) (benzylidene)ruthenium dichloride, in a nitrogen-filled glove-box at ambient temperature in sample vials or small flasks (50 mL) equipped with magnetic stirrers. Dichloromethane employed as a polymerization solvent was prepared by distillation over CaH₂ and degassed via a freeze-pump-thaw cycle. For NMR-scale reactions the monomer (45 mg, 1.23 × 10⁻⁴ mol) in 1.8 mL of dichloromethane and initiator (1.05 mg, 1.23 × 10⁻⁶ mol) in 0.5 mL of dichloromethane were prepared in different vials, and the catalyst solution was then transferred by syringe to the monomer solution. The reaction mixture was stirred for 1.5 h. The reaction was terminated by the addition of two drops of butyl vinyl ether and stirred for an additional 30 minutes. The reaction mixture was then taken out of the glove-box and poured into methanol (100 mL) to precipitate the polymer. The polymer product was isolated by filtration and dried under vacuum for several hours: *M_w* = 62,500 and PDI = 1.35 (vs. linear polystyrene standards); ¹H NMR (300 MHz, CDCl₃): δ = 0.7–3.4 (br, 8H, aliphatic), 4.3–5.8 (br, 3H, olefinic and alpha to nitrogen), 6.8–7.6 (br, 7H, aromatic), 7.8–8.2 (br, 1H, aromatic).

Block Copolymerization of *endo*-5-(9-Carbazolyl)-*trans*-6-methyl-2-norbornene and *endo*-5-[9-(3'-Bromocarbazolyl)]-*trans*-6-methyl-2-norbornene

Solutions of the catalyst RuCl₂(=CHPh)(PCy₃)₂ (68 mg, 8.02 × 10⁻⁵ mol) in 3 mL of dichloromethane and the first monomer, *endo*-5-(9-carbazolyl)-*trans*-6-methyl-2-norbornene (1.12 g, 4.10 × 10⁻³ mol), in 12 mL of dichloromethane were prepared in different flasks in a nitrogen-filled glove-box. The catalyst solution was injected into the monomer solution by syringe. The reaction was carried out at ambient temperature for 1.25 h. To obtain the block copolymer, the second monomer, *endo*-5-[9-(3'-bromocarbazolyl)]-*trans*-6-methyl-2-norbornene (723 mg, 2.05 × 10⁻³ mol) was injected into the still-living reaction mixture, and the solution was stirred continuously for another 2 h before termination as described above. The polymer was precipitated in methanol. The precipitate was collected by filtration, dried, re-dissolved in dichloromethane and re-precipitated by dropwise addition of a concentrated solution into a vigorously stirred excess of methanol. This procedure was done one more time, and the polymer products were isolated by filtration and dried under vacuum at room temperature; yield: 1.72 g (93%); *M_w* = 36,400 and PDI = 1.50 (vs. linear polystyrene standards); ¹H NMR (300 MHz, CDCl₃): δ = 0.7–3.4 (br), 4.3–5.8 (br), 6.9–7.6 (br), 7.8–8.2 (br); ¹³C NMR (500 MHz, CDCl₃): δ = 15.4, 16.8, 38.5, 41.0, 41.9, 43.3, 49.1, 65.9, 108.7, 111.5–112.5 (complex multiplicity), 118.6, 120.1, 122.7, 123.7, 125.2, 130.6, 133.1, 139.9, 141.9.

Formylation of the Block Copolymer

A stirred solution of 1.65 g of block copolymer in 30 mL of dry benzene was kept at room temperature while 2.6 mL of *n*-butyllithium [based upon a 100% conversion of the 9-(3'-bromocarbazolyl) group] was added during 15 minutes. After 3 h at this temperature, 0.32 mL of *N,N*-dimethylformamide was slowly added and the solution stirred for another 5 h. The reaction mixture was carefully quenched by the addition of saturated NH₄Cl at 0 °C, until the solution became acidic. After extraction with dichloromethane, the solution was washed successively with water, with saturated NaHCO₃ and with saturated NaCl solution. After drying over anhydrous Na₂SO₄, the solvent was evaporated to provide the corresponding carbonyl product. The polymer products were dissolved in dichloromethane and precipitated by dropwise addition of a concentrated solution into a vigorously stirred excess of methanol. The precipitate was isolated by filtration and dried under vacuum at room temperature. This procedure was done two more times; yield: 1.52 g (87.5%); *M_w* = 46,100 and PDI = 1.71 (vs. linear polystyrene standards); ¹H NMR (300 MHz, CDCl₃): δ = 0.7–3.4 (br), 4.3–5.8 (br), 6.9–7.6 (br), 7.8–8.2 (br), 9.9–10.2 (br); ¹³C NMR (500 MHz, CDCl₃): δ = 15.4, 16.7, 38.5, 41.0, 41.9, 43.3, 48.8, 65.8, 108.7, 111.6–112.5 (complex multiplicity), 118.5, 120.1, 122.7, 123.7, 125.5, 130.6, 133.1, 139.9, 141.9, 191.5; UV (dichloromethane): λ_{max} = 266, 295, 346 nm.

Introduction of the NLO Functionality into the Block Copolymer

To a mixture of malononitrile (0.15 mL) and dry pyridine (0.2 mL) in 30 mL of dry benzene stirred at ambient temperature for 30 minutes under nitrogen the previous block copolymer containing the aldehyde functionality (1.42 g) was added. The reaction mixture was heated under reflux for 22 h and cooled to room temperature followed by washing with water, drying with sodium sulfate and evaporating. The polymer products were dissolved in dichloromethane and precipitated by dropwise addition of a concentrated solution into a vigorously stirred excess of hexane. The precipitate was collected by filtration, dried, re-dissolved in dichloromethane and re-precipitated by dropwise addition of a concentrated solution into a vigorously stirred excess of hexane. The precipitate was isolated by filtration and dried under vacuum at room temperature. This procedure was done three more times to give the product; yield: 1.49 g (81%); $M_w = 42,000$ and $PDI = 3.01$ (vs. linear polystyrene standards); 1H NMR (300 MHz, $CDCl_3$): $\delta = 0.7-3.4$ (br), $4.3-5.8$ (br), $7.0-7.6$ (br), $7.8-8.3$ (br); ^{13}C NMR (500 MHz, $CDCl_3$): $\delta = 15.4, 16.6, 38.5, 41.0, 41.8, 43.3, 49.0, 65.8, 108.7, 111.5-112.5$ (complex multiplicity), $118.6, 119.8, 122.6, 123.7, 125.0, 125.5, 130.7, 133.1, 139.9, 141.9$; IR (KBr pellet): $\nu = 1596$ ($\nu_{C=C}$, aromatic), 1626 ($\nu_{C=C}$, alkene), 2223 cm^{-1} ($\nu_{C\equiv N}$, nitrile); UV (dichloromethane): $\lambda_{max} = 266, 295, 331, 346, 413\text{ nm}$; T_g 242.1°C under nitrogen and T_d (onset, 0.6 wt% loss) 368.4°C under nitrogen.

Random Copolymerization of *endo*-5-(9-Carbazolyl)-*trans*-6-methyl-2-norbornene and *endo*-5-[9-(3'-Bromocarbazolyl)]-*trans*-6-methyl-2-norbornene

A solution of catalyst $RuCl_2(=CHPh)(PCy_3)_2$ (68 mg, 8.02×10^{-5} mol) in 3 mL of dichloromethane and the mixture of monomers, *endo*-5-(9-carbazolyl)-*trans*-6-methyl-2-norbornene ($1.12\text{ g}, 4.10 \times 10^{-3}$ mol) and *endo*-5-[9-(3'-bromocarbazolyl)]-*trans*-6-methyl-2-norbornene ($723\text{ mg}, 2.05 \times 10^{-3}$ mol), in 12 mL of dichloromethane were prepared in different flasks in nitrogen-filled glove-box. The catalyst solution was injected into the monomer solution by syringe. The reaction was carried out at ambient temperature for 3.25 h before termination as described above. The polymer was precipitated in methanol. The precipitate was collected by filtration, dried, re-dissolved in dichloromethane and re-precipitated by dropwise addition of a concentrated solution into a vigorously stirred excess of methanol. This procedure was done one more time, and the polymer products were isolated by filtration and dried under vacuum at room temperature; yield: 1.81 g (98%); $M_w = 31,600$ and $PDI = 1.35$ (vs. linear polystyrene standards); 1H NMR (300 MHz, $CDCl_3$): $\delta = 0.7-3.4$ (br), $4.3-5.8$ (br), $7.0-7.6$ (br), $7.8-8.3$ (br); ^{13}C NMR (500 MHz, $CDCl_3$): $\delta = 15.4, 16.8, 37.9-39.5$ (complex multiplicity), $41.0, 41.9, 43.6, 49.0, 65.8, 108.7, 111.6-112.5$ (complex multiplicity), $118.7, 120.1, 122.7, 123.7, 125.1, 128.2, 130.7, 133.0, 139.8, 141.9$.

Formylation of the Random Copolymer

A stirred solution of 1.73 g of random copolymer in 30 mL of dry benzene was kept at room temperature while 2.6 mL of *n*-

butyllithium [based upon a 100% conversion of the 9-(3'-bromocarbazolyl) group] was added during 15 minutes. After 3 h at this temperature, 0.32 mL of *N,N*-dimethylformamide was slowly added and the mixture stirred for another 5 h. The reaction mixture was carefully quenched by the addition of saturated NH_4Cl at 0°C , until the solution became acidic. After extraction with dichloromethane, the solution was washed successively with water, with saturated $NaHCO_3$ and with saturated $NaCl$ solution. After drying over anhydrous Na_2SO_4 , the solvent was evaporated to provide the corresponding carbonyl product. The polymer products were dissolved in dichloromethane and precipitated by dropwise addition of a concentrated solution into a vigorously stirred excess of methanol. The precipitate was isolated by filtration and dried under vacuum at room temperature. These procedures were done two more times to give the product; yield: 1.40 g (80.1%); $M_w = 43,700$ and $PDI = 1.57$ (vs. linear polystyrene standards); 1H NMR (300 MHz, $CDCl_3$): $\delta = 0.7-3.4$ (br), $4.3-5.8$ (br), $7.0-7.6$ (br), $7.8-8.4$ (br), $10.0-10.3$ (br); ^{13}C NMR (500 MHz, $CDCl_3$): $\delta = 15.4, 16.8, 37.9-40.0$ (complex multiplicity), $41.1, 41.9, 43.3, 49.1, 65.8, 108.7, 111.5-112.5$ (complex multiplicity), $118.7, 120.1, 122.7, 123.7, 125.1, 130.6, 133.0, 139.9, 141.9, 191.5$; UV (dichloromethane): $\lambda_{max} = 266, 295, 346\text{ nm}$.

Introduction of the NLO Functionality into the Random Copolymer

To a mixture of malononitrile (0.15 mL) and dry pyridine (0.2 mL) in 30 mL of dry benzene stirred at ambient temperature for 30 minutes under nitrogen the previous random copolymer (1.30 g) was added. The reaction mixture was heated under reflux for 22 h and cooled to room temperature followed by washing with water, drying with sodium sulfate and evaporating. The polymer products were dissolved in dichloromethane and precipitated by dropwise addition of a concentrated solution into a vigorously stirred excess of hexane. The precipitate was collected by filtration, dried, re-dissolved in dichloromethane and re-precipitated by dropwise addition of a concentrated solution into a vigorously stirred excess of hexane. The precipitate was isolated by filtration and dried under vacuum at room temperature. These procedures were done three more times to give the product; yield: 1.24 g (67.6%); $M_w = 44,100$ and $PDI = 1.62$ (vs. linear polystyrene standards); 1H NMR (300 MHz, $CDCl_3$): $\delta = 0.7-3.4$ (br), $4.3-5.8$ (br), $7.0-7.6$ (br), $7.8-8.3$ (br); ^{13}C NMR (500 MHz, $CDCl_3$): $\delta = 15.4, 16.8, 36.5-39.4$ (complex multiplicity), $41.1, 41.9, 43.6, 49.2, 65.8, 108.7, 111.5-112.5$ (complex multiplicity), $118.8, 120.0, 122.6, 123.7, 125.5, 130.6, 133.0, 139.9, 141.9$; IR (KBr pellet): $\nu = 1594$ ($\nu_{C=C}$, aromatic), 1624 ($\nu_{C=C}$, alkene), 2223 cm^{-1} ($\nu_{C\equiv N}$, nitrile); UV (dichloromethane): $\lambda_{max} = 266, 295, 331, 346, 415\text{ nm}$; T_g 238.5°C under nitrogen and T_d (onset, 1.4 wt% loss) 374.0°C under nitrogen.

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