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Facile Synthesis of Flexible, Donor−Acceptor Side-Chain Functionalized Copolymers via Ring-Opening Metathesis Polymerization

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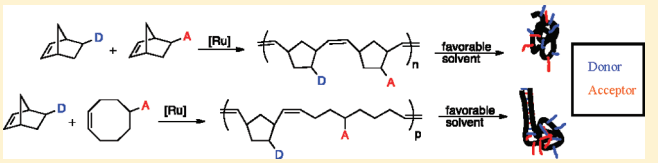
Supporting Information

ABSTRACT: A series of polymers has been synthesized via ring-opening metathesis polymerization of donor−acceptor side-chain functionalized monomers. The backbones of the polymers are based on poly(norbornene)s and/or poly(cyclooctene)s, while the side-chains consist of electron-rich 1,5-dialkoxynaphthalene and electron-deficient 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic dianhydride). The monomers were proven to be living which allowed for the generation of controlled homopolymers and block copolymers. Side-chain functionalized alternating poly(norbornene/cyclooctene)s were generated using a Grubbs-type initiator containing an unsymmetrical N-heterocyclic carbene ligand. Using UV−vis spectroscopy, a charge-transfer band was detected in random and alternating copolymer solutions due to intramolecular interactions.



INTRODUCTION

Nature uses a set of noncovalent interactions that drive the folding of biopolymers. When starting from any higher energy configuration, biopolymers assume their native state of minimal conformational energy by specific interactions between the main- and side-chains of the uniquely sequenced biopolymer backbone.[1] From these specific conformations, many functions are carried out such as molecular recognition, information storage, and catalysis.[2] In attempts to mimic this correlation of structure to function, much effort has been dedicated toward applying biological folding principles toward synthetic polymer systems.[3−7] Since polymers allow for the realization of materials[8] with interesting properties,[9−11] well-defined 3D polymeric architectures will be an important stepping-stone to the development of the next generation of functional materials.

Current synthetic 'foldamers'[12] have been employed in a range of applications, such as host−guest systems[13] and optoelectronics.[14,15] Many synthetic polymeric foldamers are driven to secondary structures by taking advantage of the inherent shape arising from rigid polymer backbones[16−18] or by strategically prepositioning recognition units as part of the backbone of the polymer.[14,15,19−24] Increasing the flexibility of the polymeric backbone and exploiting supramolecular interactions between side-chain functional groups possess the possibility to increase the utility of foldameric structures, similar to biomacromolecules. To overcome current limitations in synthetic foldamers and to expand the scope of the existing systems, it is important to develop new methods to fold flexible high molecular weight polymers; that is, polymers without any conformational constraints in the main-chain. In this contribution we report a first step toward this goal by describing a new and versatile set of living, donor−acceptor side-chain functionalized monomers that can generate a variety of random coil homo- and copolymers and study the donor−acceptor interactions between side-chains, a prerequisite to obtain folded structures.

Iverson and co-workers have described synthetic foldamers utilizing donor−acceptor interactions in what they term "aedemers" (aromatic electron donor-acceptor).[25] They have demonstrated the ability of donor−acceptor inter- and intrachain interactions to drive polymers to fold into specific secondary structures, including tweezer-like conformations.[19,25−29] Specifically, they demonstrated the assembly of two side-chain functionalized homopolymers into thread-like arrangements due to side-chain interactions between an electron-rich 1,5-dialkoxynaphthalene (Dan) and an electron-deficient 1,4,5,8-naphthalene tetracarboxylic diimide (Ndi).[26] This was confirmed through atomic-force, optical and scanning-electron microscopies. The polymers used by Iverson and co-workers were functionalized in a postpolymerization fashion. A functional group and living polymerization method, as described here, would allow for a high degree of control during the polymerization as well as complete side-chain functionalization.

This report describes a facile synthesis of controlled, flexible, side-chain functionalized polymers, including homopolymers, random copolymers, block copolymers, and alternating copolymers. The polymer backbone is synthesized via ring-opening metathesis polymerization (ROMP) of norbornenes and cyclooctenes. ROMP is a living polymerization method, allowing for control over the molecular weight of polymers and the synthesis of block and alternating copolymers.[30,31] The driving force designed into the polymers to obtain aggregates and potentially secondary structures arises from donor−acceptor functional groups along the side-chains, electron-rich 1,5-dialkoxy-naphthalene and electron-deficient 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic dianhydride).

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This pair allows for directed noncovalent interactions between complementary units. We also report the first highly functionalized alternating copolymerization of two different monomers via ROMP.

EXPERIMENTAL SECTION

General. All reactions were carried out under an inert atmosphere of either nitrogen or argon using standard vacuum and Schlenk techniques or in a glovebox under an atmosphere of N_2. All reagents were purchased either from Acros Organics, Sigma-Aldrich, EMD Chemicals, or Alfa Aesar Chemicals and used without further purification unless otherwise noted. Hexanes, toluene, and tetrahydrofuran (THF) were distilled over Na/benzophenone. Methylene chloride (CH_2Cl_2), acetonitrile, and deuterated chloroform ($CDCl_3$) were distilled over calcium hydride. Grubbs' first-generation initiator was purified by filtration using purified benzene under an atmosphere of argon. ^{1}H NMR spectra were recorded at 25 °C on a Bruker AC 400 (^{1}H: 400.1 MHz) spectrometer. ^{13}C NMR spectra were obtained at 125.0 MHz on a Bruker AC 500 spectrometer. Chemical shifts are reported in parts per million (ppm) with reference to solvent residual nuclei in deuterated solvents. Molecular weights and polydispersity indices were measured using a Shimadzu pump coupled to a Shimadzu UV detector with THF as the eluant and a flow rate of 1 mL/min on American Polymer Standards column set (100, 1000, 100 000 Å, linear mixed bed). All GPCs were calibrated using poly(styrene) standards and carried out at 25 °C. M_w, M_n, and PDI represent the weight-average molecular weight, number-average molecular weight, and polydispersity index, respectively. Bicyclo[2.2.1]hept-5-ene-exo-2-carboxylic acid (norbornene-exoacid) (**4**)[32] was synthesized according to literature procedure.

*2-((5-(Hexyloxy)Naphthalen-1-yl)oxy)ethanol (**3**).* To a solution of 1,5-dihydroxynaphthalene **1** (10.0 g, 49 mmol) in acetonitrile (100 mL) were added K_2CO_3 (15.7 g, 109 mmol), bromohexane (8.1 g, 49 mmol), and KI (cat). The mixture was stirred under refluxed for 18 h and then cooled to room temperature. The solid was filtered off, and the solution was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (10 mL) and washed with dilute hydrochloric acid (10 mL), water (10 mL), and brine (10 mL). After drying over $MgSO_4$, the solvent was removed under reduced pressure, and the resulting residue was subjected to column chromatography (1:3 ethyl acetate (EtOAc): Hexanes) to afford **2** in 33% yield. ^{1}H NMR ($CDCl_3$): δ = 7.88 (d, J = 8.5, 1H), 7.71 (d, J = 8.5, 1H), 7.38 (t, J = 8.1, 1H), 7.29 (t, J = 7.9, 1H), 6.84 (t, J = 6.8, 2H), 4.13 (t, J = 6.4, 2H), 1.92 (dt, J = 14.5, 7.0, 2H), 1.56 (t, J = 7.4, 2H), 1.40−1.36 (m, 4H), 0.92 (t, J = 7.0, 3H); ^{13}C NMR ($CDCl_3$): δ = 155.0, 151.3, 127.3, 125.5, 125.1, 115.0, 113.4, 109.5, 105.4, 68.5, 31.9, 29.5, 26.2, 22.9, 14.3. Elemental analysis calcd % for $C_{16}H_{20}O_2$ (244.15): C 78.65, H 8.25; found: C 78.51, H 8.24.

The same procedure was then repeated using **2** (500.0 mg, 2.05 mmol), chloroethanol (0.98 mL, 1.42 mmol) in acetonitrile (10 mL), K_2CO_3 (507.6 mg, 3.52 mmol), and KI (0.25 g) and subjected to column chromatography (1:4 EtOAc:Hexanes) to afford **3** in 58% yield. ^{1}H NMR ($CDCl_3$): δ = 7.90 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.37 (ddd, J = 7.6, 4.4, 3.6 Hz, 2H), 6.85 (t, J = 8.2 Hz, 2H), 4.26 (t, J = 4.6 Hz, 2H), 4.14−4.08 (m, 4H), 2.12 (t, J = 6.4 Hz, 1H), 1.92 (m, 2H), 1.61−1.53 (m, 3H), 1.42−1.35 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 154.7, 154.2, 126.8, 126.6, 125.3, 124.9, 114.8, 113.8, 105.7, 105.3, 69.7, 68.2, 61.5, 31.7, 29.3, 26.0, 22.6, 14.0 Elemental analysis calcd % for $C_{18}H_{24}O_3$ (288.17): C 74.97, H 8.39; found: C 74.82, 8.41.

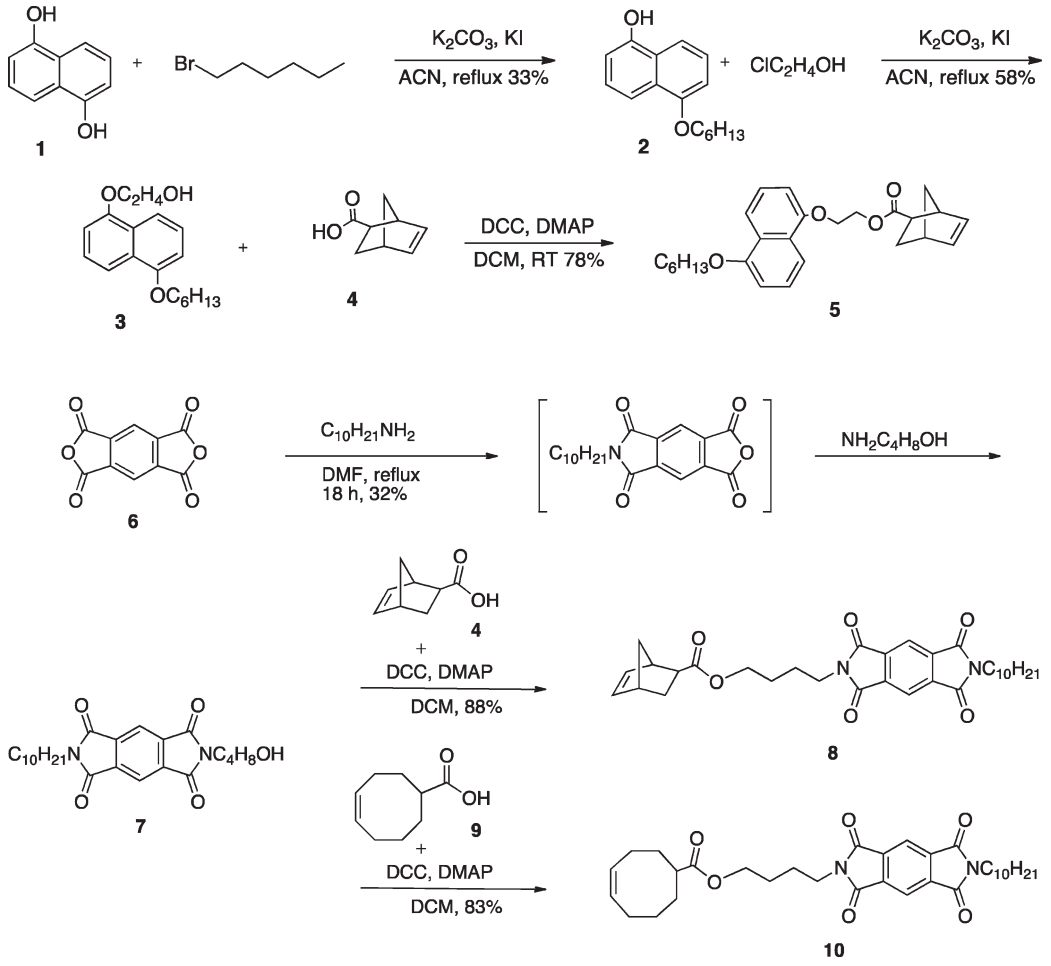
*2-(1-(Hexyloxy)naphthalene-5-yloxy)ethyl-norbor-5-ene-2-carboxylate (**5**).* Dialkoxynaphthalene (126.0 mg, 0.44 mmol) **3** and norbornene *exo*-acid **4** (50.3 mg, 0.36 mmol) were dissolved in (30 mL) CH_2Cl_2. A 3 mL solution of dicyclohexylcarbodiimide (DCC) (82.6 mg, 0.30 mmol) was added to the reaction mixture. A catalytic amount of 4-(dimethylamino)pyridine (DMAP) was added, and the solution was stirred at room temperature for 12 h. The mixture was concentrated under reduced pressure. The crude product was purified by column chromatography using 1:4 EtOAc:Hexanes to afford **5**. ^{1}H NMR ($CDCl_3$): δ = 7.88 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.35 (t, J = 8.1 Hz, 2H), 6.83 (d, J = 7.7 Hz, 2H), 6.12 (dd, J = 5.6, 2.9 Hz, 1H), 6.08 (dd, J = 5.6, 3.1 Hz, 1H), 4.58 (m, J = 5.7 Hz, 2H), 4.34 (t, J = 4.8 Hz, 2H), 4.11 (t, J = 6.4 Hz, 2H), 3.06 (s, 1H), 2.90 (s, 1H), 2.29−2.26 (m, 1H), 1.93 (ddt, J = 17.6, 11.6, 5.8 Hz, 4H), 1.58−1.54 (m, 5H), 1.37 (td, J = 8.4, 4.8 Hz, 8H), 0.92 (t, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ = 176.6, 154.8, 154.2, 138.1, 135.8, 127.0, 126.8, 125.4, 124.9, 115.0, 114.1, 105.8, 105.5, 68.3, 66.6, 62.8, 46.8, 46.5, 43.2, 41.8, 31.7, 30.5, 29.4, 26.1, 22.7, 14.2. Elemental analysis calcd % for $C_{26}H_{32}O_4$ (408.23): C 76.44, H 7.90, O 15.67; found: C 76.04, H 8.01, O 15.95.

*2-Decyl-6-(4-hydroxybutyl)pyrrolo[3,4-f]isoindole-1,3,5,7(2H,6H)-tetraone (**7**).* Pyromellitic dianhydride **6** (6.0 g, 0.028 mol) was dissolved and stirred at 150 °C. To this mixture, decylamine (4.1 mL, 0.021 mol) was added dropwise, and the solution was refluxed for 12 h. 3-Amino-1-propanol (2.1 mL, 0.028 mol) was added, and the mixture was refluxed for an additional 12 h. The solution was cooled to room temperature and concentrated under reduced pressure. The residue was dissolved in dichloromethane (30 mL) and washed with distilled water (3 × 30 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography using 1:3 EtOAc:CH_2Cl_2 to afford **7** in 32% yield. ^{1}H NMR ($CDCl_3$): δ = 8.26 (s, 1H), 3.91 (t, J = 6.5 Hz, 1H), 3.72 (t, J = 7.3 Hz, 1H), 3.65 (q, J = 5.8 Hz, 1H), 2.06 (t, J = 6.2 Hz,), 1.92 (dt, J = 12.4, 6.1 Hz, 1H), 1.68 (t, J = 6.9 Hz, 1H), 1.27 (d, J = 31.5 Hz, 7H), 0.90−0.82 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 171.4, 166.9, 166.5, 137.7, 137.4, 118.5, 60.7, 59.7, 39.1, 35.7, 32.1, 31.4, 29.8, 29.54, 29.40, 28.7, 27.1.

*3-(6-Decyl-1,3,5,7-tetraoxo-6,7-dihydropyrolo[3,4]isoindol-2-yl)-propylnorbor-5-ene-2-carboxylate (**8**).* Norbornene-*exo*-acid **4** (400.0 mg, 2.89 mmol) and **7** (1.0 g, 2.41 mmol) were dissolved in CH_2Cl_2 (20 mL). A 3 mL solution of DCC (547.0 mg, 2.65 mmol) was added to the initial reaction mixture. A catalytic amount of DMAP was added to the solution and stirred at room temperature for 12 h. The CH_2Cl_2 was evaporated under reduced pressure. The crude product was purified by column chromatography using 5% EtOAc/CH_2Cl_2 to afford **8** in 88% yield. ^{1}H NMR ($CDCl_3$): δ = 8.26 (s, 2H), 6.12 (dd, J = 5.6, 3.0, 1H), 6.06 (dd, J = 5.7, 3.1, 1H), 4.14 (t, J = 6.1, 2H), 3.87 (t, J = 6.9, 2H), 3.73 (t, J = 7.4, 2H), 3.03 (dq, J = 2.2, 0.7, 1H), 2.91 (s, 1H), 2.16 (ddd, J = 8.7, 4.5, 1.6, 1H), 2.08 (m, J = 6.5, 2H), 1.91 (dt, J = 11.7, 4.0, 1H), 1.52−1.50 (m, 1H), 1.38−1.28 (m, 18H), 0.87 (t, J = 6.9, 3H).

*4-(6-Decyl-1,3,5,7-tetraoxo-6,7-dihydropyrrolo[3,4-f]isoindol-2-(1H,3H,5H)-yl)butylcyclooct-4-enecarboxylate (**10**).* Cyclooctene-acid **9** (753.0 mg, 2.10 mmol) and **7** (270.0 mg, 1.75 mmol) were dissolved in CH_2Cl_2 (15 mL). A 3 mL solution of DCC (397.2 mg, 1.93 mmol) was added to the initial reaction mixture. A catalytic amount of DMAP was added, and the solution was stirred at room temperature for 12 h. The CH_2Cl_2 was evaporated under reduced pressure. The crude product was purified by column chromatography using 5% EtOAc/CH_2Cl_2 to afford **10** in 83% yield. ^{1}H NMR ($CDCl_3$): δ = 8.26 (s, 1H), 5.67−5.55 (m, 1H), 8.26−0.85 (m, 1H), 4.11−4.09 (m, 1H), 3.85 (t, J = 6.9 Hz, 1H), 3.73 (t, J = 7.3 Hz, 1H), 2.40−2.31 (m, 1H), 2.12 (q, J = 6.5 Hz, 1H), 2.06 (dd, J = 13.0, 6.7 Hz, 1H), 2.00 (t, J = 3.8 Hz, 1H), 1.97 (t, J = 3.8 Hz, 1H), 1.82 (td, J = 14.2, 3.5 Hz, 1H), 1.69 (dt, J = 7.5, 3.6 Hz, 1H), 1.63−1.49 (m, 1H), 1.32−1.24 (m, 1H). ^{13}C NMR ($CDCl_3$): δ = 177.5, 166.3, 137.5, 137.2, 130.6, 129.6, 118.3, 61.6, 43.4, 38.9, 36.0, 32.0, 31.6, 29.64, 29.60, 29.5, 29.4, 29.2, 28.5, 27.9, 27.6, 26.9, 26.0, 24.2, 22.8, 14.2. Elemental analysis calcd % for $C_{26}H_{32}O_4$ (550.69): C 69.79, H 7.69, N 5.09, O 17.43; found: C 69.79, H 7.78, N 5.06, O 18.06.

Scheme 1. Synthesis of Monomers 5, 8, and 10



General Polymerization Procedure. The desired quantity of monomer(s) **5** and **8** (for $\mathbf{P_1}$ and $\mathbf{P_2}$) was dissolved in degassed chloroform under an argon atmosphere. A solution of Grubbs' first generation initiator in degassed chloroform was added and stirred at 25 °C. Upon completion of the polymerization, ethyl vinyl ether was added, and the reaction was stirred at 25 °C for 1 h. Each polymer was precipitated into MeOH three times and dried under high vacuum.

$\mathbf{P_3}$. Following the general procedure for $\mathbf{P_1}$, upon complete polymerization of the preceding monomer (as determined by ^{1}H NMR monitoring) the subsequent monomers were added at their appropriate times. After the complete polymerization of the final monomer, ethyl vinyl ether was added, and the reaction was stirred at 25 °C for 1 h.

$\mathbf{P_4}$. To a solution of **5** (10.4 mg, 0.025 mmol) and **10** (700.0 mg, 1.27 mmol) in anhydrous CH_2Cl_2 (2.0 mL) were added **11** (0.39 mg, 5.08 10^{-4} mmol) and (cat.) CuCl. The mixture was stirred at 25 °C for 10 min, and then the polymerization was quenched with addition of ethyl vinyl ether, allowed to stir at 25 °C for 1 h, and then precipitated in MeOH three times. The resulting polymer was further purified via size exclusion chromatography using 1:1 chloroform: methanol eluant.

RESULTS

Monomer Synthesis. Monomers **5**, **8**, and **10** were synthesized as outlined in Scheme 1. *exo*-Norbornene carboxylic acid **4** and cyclooctene carboxylic acid **9** were synthesized according to literature procedures.[32] The norbornene-based donor monomer **5** was synthesized via two Williamson ether syntheses on **1**, followed by standard DCC/DMAP coupling to **4**. The acceptor monomer side-chains were synthesized by a one-pot addition of two different amines to pyromellitic dianhydride **6**, followed by standard DCC/DMAP couplings to either **4** or **9** to complete the norbornene-based and cyclooctene-based acceptor monomers, respectively.

Living Polymerization Studies. For the synthesis of our target copolymers, we evaluated the living character of the ROMP of norbornene monomers **5** and **8**. Each monomer was subjected to ROMP using Grubbs' first-generation initiator at 25 °C in degassed chloroform. Initially, **5** and **8** were polymerized at various monomer to initiator ratios ([M]:[I] = 20:1, 40:1, 60:1, 80:1, 100:1). Gel-permeation chromatograms of each polymer ratio were taken (Figure 1), and the M_n vs [M]:[I] ratios were plotted. For both monomers, a linear relationship was obtained suggesting a high degree of control over the polymerization.

We also monitored the signal of the alkylidene of the ruthenium catalyst during the polymerizations by ^{1}H NMR spectroscopy. A complete shift from 19.9 ppm to 18.7 ppm was observed, and the signal remained constant during the duration of the polymerization. These data strongly indicate that the ruthenium complexes had fully initiated and that the resulting catalysts stayed active throughout the polymerization.

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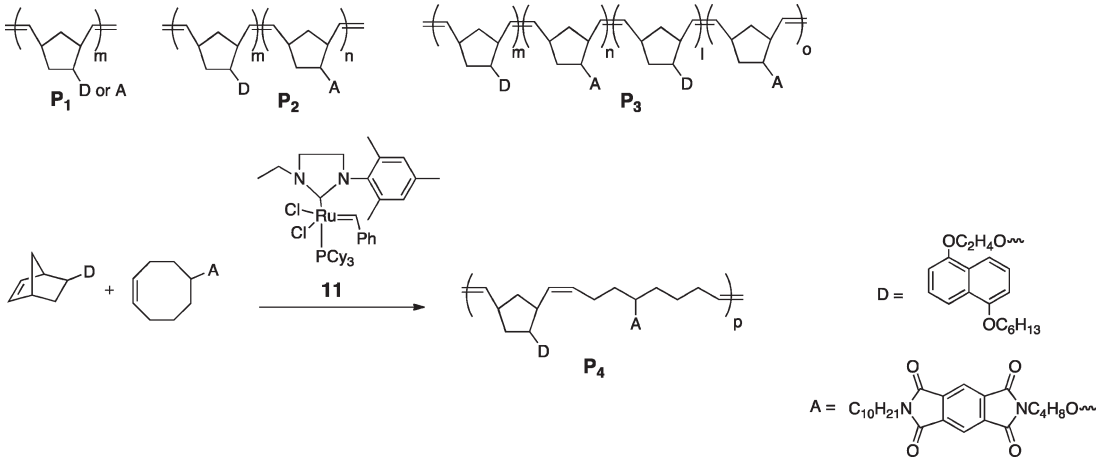
Scheme 2. Illustration of Synthesized Polymers: Homopolymer P_1, Random Copolymer P_2, Block Copolymer P_3, and Alternating Copolymer P_4



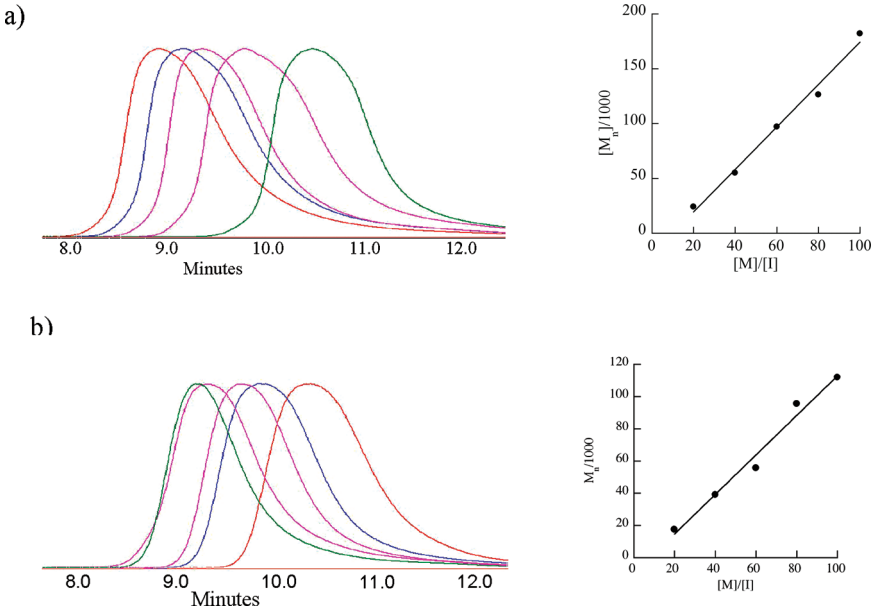


Figure 1. Living polymerization tests of **5** and **8**. a) GPC spectra of **5** using [M]:[I] ratios of 20:1, 40:1, 60:1, 80:1, 100:1; b) GPC spectra of **8** using [M]:[I] ratios of 20:1, 40:1, 60:1, 80:1, 100:1.

Lastly, homoblock copolymerization experiments were conducted on both monomers. Each monomer was first polymerized at a 20:1 [M]:[I] ratio. After complete consumption of the initial batch of monomers, additional monomers were added to the reaction mixtures to obtain 100mers. The gel-permeation chromatography (GPC) data show a complete shift of the lower molecular weight acceptor (M_n = 25 000; PDI = 1.30) and donor (M_n = 15 500; PDI = 1.34) homopolymers (20mers) to higher molecular weight [(M_n = 88 600; PDI = 1.16), (M_n = 144 000; PDI = 1.24); donor, acceptor respectively] homopolymers (100mers), without a trace of the lower molecular weight polymers (**S1c** and **S2c**, respectively). These combined studies prove that both norbornene monomers polymerize in a living fashion.

After demonstrating that monomers **5** and **8** are living, we synthesized a series of random, block, and alternating copolymers. All polymers were characterized using ^{1}H NMR and ^{13}C NMR spectroscopies and GPC. The GPC results are summarized in Table 1.

We initially investigated the random copolymerization of **5** and **8** that provides for the random dispersion of donor and acceptor side-chains along the polymer. The random copolymers were synthesized by combining **5** and **8** in a 1:1 ratio with Grubbs' first generation initiator. GPC data show a unimodal distribution of the random copolymers (M_n = 73 000; PDI = 1.24).

ABAB tetrablock copolymers were synthesized using similar conditions to the block homopolymerization tests in order to see whether or not the polymers would allow for intramolecular donor−acceptor interactions to induce order in the polymer arrangement. Figure 2 shows a kinetic experiment monitoring the ABAB tetrablock polymerization via ^{1}H NMR spectroscopy, in which the olefinic monomer and polymer signals were tracked. The olefin signals for **8** (bottom spectra, Figure 2 left) decrease

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over time. Following the complete disappearance of the olefin signal of **8** and an increase of the signals for the polymer backbone double bonds (Figure 2 right), **5** was introduced to the polymerization flask. Again, the signal for the olefinic hydrogens disappeared over time. This procedure was repeated two more times until a tetrablock of **8**:**5**:**8**:**5** was synthesized. After complete polymerization of the final monomer, the polymerization was quenched with ethyl vinyl ether.

Table 1. Gel-Permeation Chromatography and UV-Vis Spectroscopy Characterization of Polymers

	[M]:[I]	$M_n(10^3)$	PDI	CT band λ (nm)
poly-**5**	20	24.0	1.47	-
	40	55.0	1.54	-
	60	97.0	1.53	-
	80	126.5	1.60	-
	100	182.0	1.60	-
poly-**8**	20	17.5	1.59	-
	40	29.0	1.55	-
	60	55.6	1.48	-
	80	95.5	1.60	-
	100	112.0	1.50	-
poly-**8**, **5**, **8**, **5**	30−30−30−30	468.0	1.66	-
random	30−30	73.0	1.24	457[a], 445[b], 437[c]
alternating	10[d]	12.0[e]	1.09[e]	460[a]

[a] $CHCl_3$. [b] THF. [c] Toluene (3 mM). [d] This value reflects the percent of the alternation of the alternating copolymer ($\mathbf{P_4}$) (see Scheme 2) determined by ^{13}C NMR spectroscopy using an inverse-gate ^{1}H decoupling experiment [% alternation = $\int$ ($\mathbf{P_4}$ signals)/$\int$ ($\mathbf{P_4}$ signals + poly-**10** signals)] (see Figure S7 in the Supporting Information). [e] These values reflect the purified polymer sample. It is possible to have a mixture of the alternating copolymer containing a block of pure poly-**10** obtained after the alternation as well as poly-**10** homopolymer. We are not able to distinguish whether the observed signals arise from homopolymer poly-**10** or a block poly-**10** tail end of the alternating copolymer.

We were interested to see whether perfectly alternating copolymers would allow for superior interactions between donor and acceptor side-chains. In contrast to random copolymers where donor and acceptor side-chains are oriented in a random fashion, we rationalized that perfectly alternating copolymers might allow for superior prealignment of side-chains thereby maximizing donor−acceptor interactions.

To date, few investigations on alternating copolymerization via ROMP have been reported.[33,34] In 2006, Blechert and coworkers reported the synthesis of two different unsymmetrical N-heterocyclic amine ligands. These ligands were coordinated to Grubbs' first-generation initiator by replacing one of the phosphine ligands.[35] In 2008, the Blechert group, in collaboration with the Buchmeiser group, applied these complexes toward the alternating copolymerization between norbornene and cyclooctene.[30] They were able to obtain up to 97% alternation according to NMR spectroscopy and thermal gravimetric analysis. However, the polymerization also generated insoluble polymers, which were found to be poly(cyclooctene) homopolymer. The monomers in those investigations were unfunctionalized.

We synthesized the Blechert complex **11** and employed it toward the homopolymerization of **5** and **10**. The homopolymerizations of **5** and **10** using **11** follow comparable rates to the ROMP using Grubbs' first-generation initiator. We then attempted the alternating copolymerization using a ratio of 1:50 between **5** and **10**, following literature procedures.[30] Unfortunately, we were unable to obtain any alternating copolymers. We introduced CuCl as a phosphine scavenger to the reaction in order to enhance the activity of **11**. In the final material using our standard polymerization conditions plus the added phosphine scavenger, we observed two new signals in the ^{13}C NMR spectrum (132 ppm and 127 ppm) as seen in Figure 3, and no signal corresponding to the norbornene homopolymer suggesting that all norbornene monomers must have been incorporated into the polymer in an alternating fashion.

In order to attribute the new signals in the ^{13}C NMR spectra to alternating copolymers and to exclude the possibility of coordination of the copper chloride to the aromatic protons of

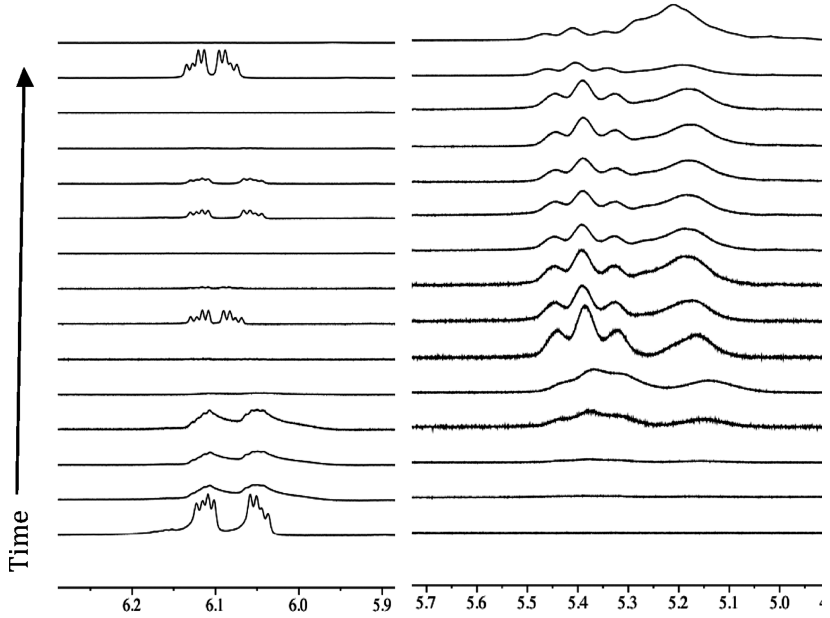

Figure 2. Partial ^{1}H NMR spectra of poly(**8**,**5**,**8**,**5**): Olefin region of the norbornene (left) and polymer (right) during the polymerization progress.

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the side-chains, we performed the homopolymerization of both monomers again using **11** with the addition of CuCl. The ^{13}C NMR signals at 132 ppm and 127 ppm were not present in either of the spectra. Next, we performed the alternating copolymerizations using a different phosphine scavenger, $AlCl_3$. Again, the new signals appeared. These data strongly suggest that we have achieved successfully a segment of alternating copolymers of two highly functionalized monomers.

UV−Vis Spectroscopy. After synthesizing random, block and alternating copolymers, we investigated whether or not the donor and acceptor side-chains interact through intrachain charge-transfer. This intrachain charge transfer could align the complementary units and force the polymers into secondary structures. As a control experiment, we prepared mixed monomer and polymer solutions (the following compounds were investigated: monomers **5** and **8**, a 1:1 mixture of **5**/**8**, and a 1:1 mixture of **poly-5**/**poly-8**) at different concentrations to observe whether or not charge-transfer bands were detectable in the UV−vis spectra.[21,22,36,37] All samples were absent of any charge-transfer signals within the reported spectral ranges as seen in Figure 4a, where all of the aforementioned solution traces remained at the baseline of the spectra. The absence of a charge-transfer band within all of the spectra is attributed to the low association constants reported for the Dan-pyromellitic dianhydride complex ($300 \leq K_a \leq 1200\ M^{-1}$ in $CHCl_3$)[37] and the entropic penalty for a stacked arrangement of side-chains from multiple monomers or polymers. Tetrablock copolymer poly-**8**,**5**,**8**,**5** was also tested at various concentrations (70 μM to 5 mM) and did not show any detectable charge-transfer signals.

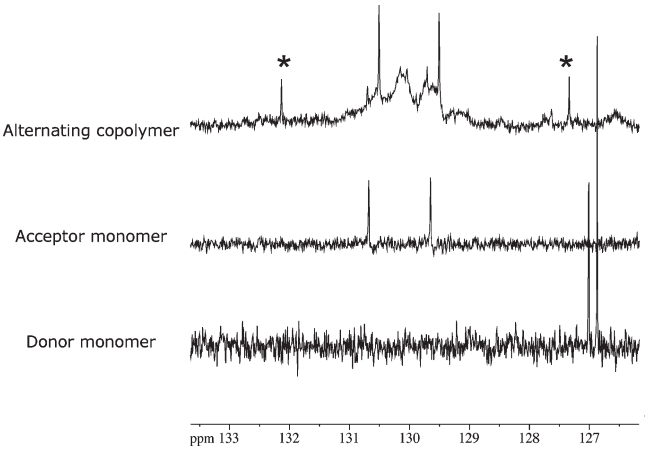

Figure 3. Partial ^{13}C NMR spectrum of **5**, **10**, poly-**5**, poly-**10**, and the alternating copolymer $\mathbf{P_4}$. Signals between 129 ppm and 131.5 ppm correspond to the polymer backbone signals of poly-**10**. The two sharp signals at 129.5 ppm and 131 ppm are from residual monomer **10**, which was not possible to be removed from the polymers despite multiple precipitations and size-exclusion column chromatography. The asterisk denotes the signals for the polymer signals of the alternating copolymer. All other unmarked signals correspond to monomer signals.

Next, we investigated the random copolymer systems by UV−vis spectroscopy. We expected an increase in the probability of complementary donor−acceptor side-chain interactions along the polymer chain due to the close proximity of the side-chains along a single polymer backbone. A new signal was detected at ~450 nm, within the range reported for the charge-transfer interaction of these moieties (Figure 4a).[21,22,36,37] In order to determine whether these interactions resulted from inter- versus intramolecular interactions, a concentration study was carried out varying the concentration from 70 μM to 5 mM. The signal was persistent and follows the expected Beer−Lambert behavior as shown in Figure 4b. This proved that the charge-transfer is occurring intramolecularly.

In order to evaluate whether a change of solvent can be utilized to effect the interactions between the donor−acceptor units in the random copolymer, i.e. whether a solvophobic effect can be detected, we attempted to dissolve it in an array of solvents of varying polarities. The copolymers were only soluble in chloroform, tetrahydrofuran, and toluene. Figure 5 shows the partial UV−vis spectra of the random copolymers in these three solvents.

We observed a shift in the charge-transfer band with the change in solvent polarity.[38] The polymer dissolved in the more polar solvent chloroform (Figure 5), exhibited the most red-shifted charge transfer band at ~460 nm, signifying a more favorable orientation of the aromatic units. The effect from toluene solution, however, is understood by looking at the monomeric region of the UV−vis spectrum (Supporting Information **S4**). There is clearly a significant red-shift of the monomer signals (from 200 to 400 nm). We attribute this result to the

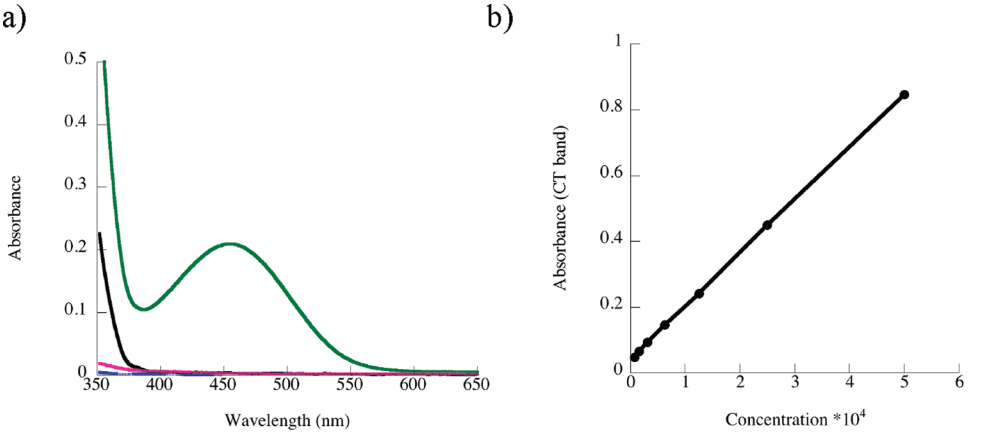

Figure 4. Partial UV−vis spectra of the charge-transfer region in chloroform (3 mM). a) Comparison of monomers, mixed monomers (1:1), mixed homopolymers (40mers; 1:1), random copolymer (40mer), and blocky copolymer (120mer). The green trace is the random copolymer spectrum. All other spectra remain at the baseline. b) Variation of charge-transfer absorbance against concentration of the random copolymer in chloroform.

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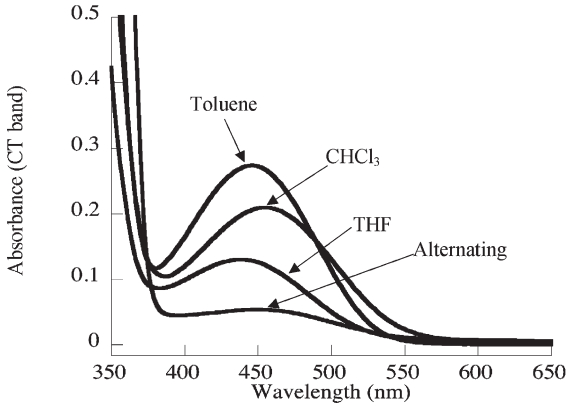

Figure 5. Partial UV−visible spectra of 3 mM random copolymer solutions in toluene, THF, and chloroform as well as a 3 mM solution of the alternating copolymers in $CHCl_3$.

conjugation between the aromatic units of the solvent and the monomer side-chains.[39]

Similar to the random copolymers, the alternating copolymer chloroform solution also shows a charge-transfer absorbance band in the reported spectral range. These results are further discussed in the Discussion section below.

DISCUSSION

Several polymers were synthesized with the desire to study the charge transfer interactions between the side-chain units of the polymers and were characterized by UV−vis spectroscopy. The low association constants reported for the Dan-pyromellitic dianhydride complex resulted in an absence of a charge-transfer band absorption in the UV−vis spectroscopy experiments of the combined 1:1 homopolymer solutions and the blocky copolymer solutions (Figure 4a). The random copolymer and alternating copolymer solutions, however, both exhibited a charge-transfer absorbance signal at ∼460 nm.

While the random copolymers in this study are composed of two norbornene-based monomers, the alternating copolymers were synthesized from the copolymerization of one norbornene-based monomer and one cyclooctene-based monomer. Varying the distance between interacting units of a charge-transfer pair can have a significant effect on the orbital alignment of the donor and acceptor charge-transfer interactions.[40] Looking at the fully norbornene-based polymers versus the norbornene-cyclooctene based alternating copolymer, there is a significant difference in the distance between the donor and acceptor units along the side-chains of the polymers. The side-chains along the poly(norbornene) are spaced between 3 and 4 carbons, whereas in the poly(norbornene-cyclooctene) system the side-chains are spaced apart by 5 to 6 carbons. During the polymerization of the functionalized norbornene monomers, each monomer can add either in a head-to-tail, head-to-head, or a tail-to-tail symmetry resulting in a lack of regiospecificity during the polymerization. This difference in spacing between the poly(norbornene) versus poly(cyclooctene) can significantly effect the alignment of the side-chain units and thus can directly influence the charge-transfer absorbance detectable by UV−vis spectroscopy as seen in Figure 5.[40,41] Furthermore, the 50 fold excess of cyclooctene monomer resulted in the formation of cyclooctene homopolymer and/or long poly(cyclooctene) runs in the copolymers as seen in the ^{13}C NMR spectra. We suggest that these combined structural features resulted in a lower charge transfer absorbance band for the alternating copolymers.

CONCLUSION

In summary, we have introduced a new versatile set of living donor−acceptor side-chain functionalized monomers that were used to generate a variety of homo- and copolymers including block copolymers, random copolymers, and alternating copolymers. Characterization of the polymers by UV−vis spectroscopy shows a charge-transfer absorption band for the random and alternating copolymers. We elucidated that intrachain and not interchain interactions between the donor and acceptor side-chain units are the reason for the charge-transfer band. The described alternating materials are the first to be synthesized from highly functionalized monomers via ROMP. This work is a step forward toward increased control over secondary structure for future functional materials.

ASSOCIATED CONTENT

Supporting Information. ^1H NMR spectra of monomers, monomer living test results, additional UV−vis spectra, and ^1H NMR titration data. This material is available free of charge via the Internet at http://pubs.acs.org.

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