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Controlling the Orientation of Pendants in Two-Dimensional Comb-Like Polymers by Varying Stiffness of Polymeric Backbones

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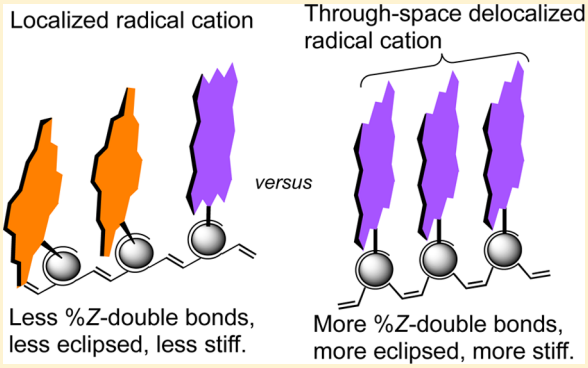
Supporting Information

ABSTRACT: The electronic communications between chromophores are closely related to distances and orientation of these π-conjugated systems. Reported herein is a collection of well-defined two-dimensional comb-like polymers containing porphyrin pendants obtained by ring-opening metathesis polymerizations of norbornene and cyclobutene derivatives using ruthenium or molybdenum catalysts. The spacing separating the adjacent pendants are defined by ring sizes of cycloalkenes and the orientations are determined by the stiffness of the polymeric backbone, which is, in turn, discerned by the percentage of *Z*-double bonds. Both peak widths of the porphyrin radical cation of the EPR spectra and the absorption profiles in the Soret band region reflect the degree of the spin delocalization and exciton coupling between porphyrin pendants in these polymers and, hence, the stiffness of the polymeric backbone. Our approach offers a useful protocol to align an array of chromophores appended onto a rigid polymeric backbone so that the optoelectronic properties can be tuned.



INTRODUCTION

Intrachain exciton and electron migrations between chromophores appended to a polymeric backbone[1−8] or associated with a supramolecular scaffold[9,10] have offered useful models to understand various natural light harvesting processes. These photophysical routes are known to be sensitive to distance and orientation of chromophores.[11] Flexible polymeric framework, such as polystyrene,[1,2] poly(methyl methacrylate)[3] polypeptides,[4] and polymers derived from dibenzofulvenes[5] are frequently used. Conformational disorder arising from rotatory single bonds may lead to irregular microstructures on the backbone. The control over the position of pendants in two-dimensions relies on the use of a more rigid scaffolds including oligoproline,[4] nucleic acid,[6] polyisocyanides[7] and polynorbornenes.[8,12−17] Accordingly, interactions between pendant chromophores would be more efficient if they could be better aligned along polymeric backbone.

Recently, polynorbornenes **1** obtained from ring-opening metathesis polymerization (ROMP) of norbornenes fused with endo-N-arylpyrrolidine moiety **2** have been shown to have isotactic stereochemistry with all pendants aligned toward a similar direction like a Chinese folded fan (eq 1).[12] These unique topological features have facilitated the successful synthesis of polynorbornene-based ladderphanes[13−15] and replication of single stranded polynorbornenes into corresponding daughter polymers.[16] The spacing separating adjacent monomeric units for these polynorbornenes is about 5.5 Å.[12] Interactions between neighboring pendants or linkers can be discerned by various spectroscopic means.[12−17] Fluorescence quenching,[14a,c,d] excimer formation,[14a] Soret band splitting,[14a,17a,b] and enhancement of chiroptical properties[13c,17b,c] and second order optical nonlinearity[12] are frequently observed in these polynorbornene-based polymers.

Thanks to the rapid development of various catalytic systems,[18−20] the stereochemistry of double bonds and the tacticity of polymers derived from the ROMP of strained cycloalkenes can be well controlled. Thus, double bonds in **1** are predominantly, if not exclusively, trans when the first generation Grubbs catalyst **3**[18] is used,[12−17] whereas Z-selectivity is obtained when the Schrock−Hoveyda catalyst **4**[19a−c,20] is employed.[21] More recently, cyclobutene derivatives **6** was transformed into polycyclobutenes **7** using **3**, **4**, or **5** as the catalyst (eq 2).[22] It is noteworthy that isotactic **7** with all double bonds in Z-configuration is obtained when **4** is employed for the ROMP reaction.[22] The span for each of the monomeric units in **7** is estimated to be around 4.5 Å.

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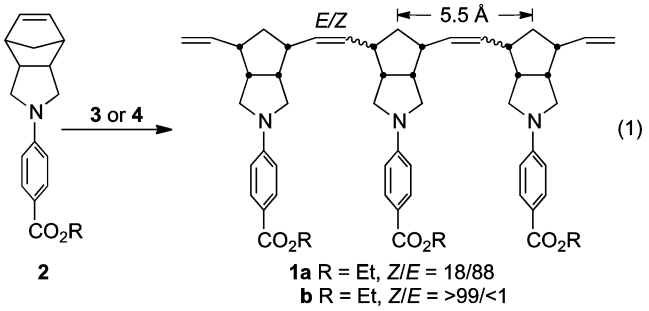
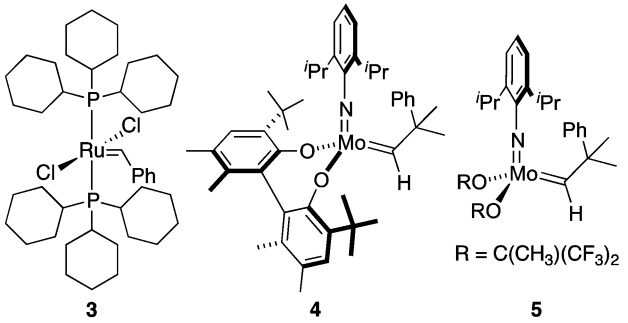
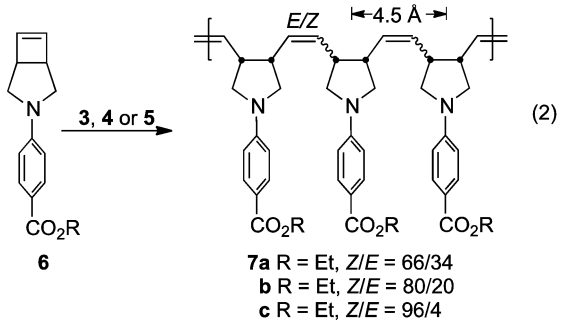


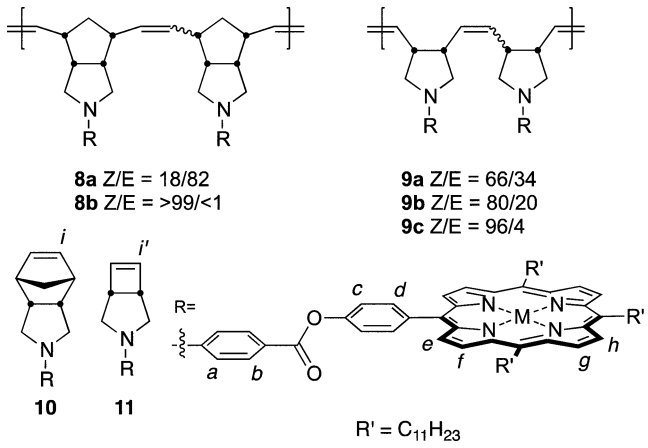




Stiff architectures such as *p*-oligophenyls,[23] oligoporphyrins,[24] and oligonaphthalenes,[25] are rigid, but noncoplanar because of torsional strain between pendants on the adjacent aromatic rings.[26] Although several approaches are documented to determine the stiffness of a polymer,[27] to the best of our knowledge, no systematic study on the influence of the structure and/or stereochemistry of the backbone on polymer stiffness. It is envisaged that tuning of the stereochemistry of the double bonds in polycycloalkenes **1** and **7** and varying the ring size of the starting cycloalkenes may be used to control the orientations of the pendants as well as the distances between adjacent chromophores appended to the polymerc backbone, and if so, influence the stiffness of the polymeric backbones.[28] Accordingly, we could study how the photophysical properties of these polymers vary with the stiffness of the polymeric backbones. In this paper, we test this idea by synthesizing a series of porphyrin-appended polynorbornenes **8** and polycyclobutenes **9** for the examination of the relationship of the physical properties and the stiffness of the backbones.

RESULTS AND DISCUSSION

Syntheses. The porphyrin-appended norbornene and cyclobutene monomers **10** and **11** were prepared according to reported procedures.[17,22,29] ROMP of **10** and **11** in the presence of **3** afforded isotactic polynorbornene **8a** (Z/*E* = 18/82) and isotactic polycyclobutene **9a** (Z/*E* = 66/34), respectively. *Z*-Isotactic polynorbornene **8b** (Z/*E* = >99/<1) and *Z*-isotactic polycyclobutene **9c** (Z/*E* = 96/4) were obtained from **10** and **11**, respectively, by using Schrock–Hoveyda catalyst **4**. On the other hand, a mixture of stereoisomeric polycyclobutene **9b** (Z/*E* = 80/20) was obtained when **5** was used. The results are summarized in Table 1. The stereochemistry of these polymers **8** and **9** were assigned on the basis of the comparison of the corresponding ethanolysis products **1** (R = Et) and **7** (R = Et), respectively, with the authentic samples prepared from **2** (R = Et) and **6** (R = Et).[29]



^{1}H NMR Spectra of 8 and 9. The ^{1}H NMR spectra of **8** and **9** are compared in Figure 1. As expected, the aromatic protons of porphyrin pendants in these polymers appear at higher field than those of monomers **10** and **11**. Interestingly, the signals for these protons shift slightly to higher field when the percentage of Z double bonds increases. In addition, the aromatic protons in **9** appear at somewhat more upfield than those in **8**. As mentioned earlier, the span for each of the monomeric unit in **1** is around 5.5 Å[12a] and that in polycyclobutenes **7** is estimated to be somewhat shorter than

Table 1. Physical Properties of Monomers and Polymers

substrate	M_n (PDI)	Et ester[a]	M_n (PDI)	% Z[b]	I_{406}/I_{419}[c]	ΔH_N[d]	N_s[e]
10	1165[f]	**2**	283	–	–	9.17	–
11	1125[f]	**6**	243	–	–	9.29	–
8a	15 300 (1.12)	**1a**	3700 (1.15)	18	1.21	8.62	1.2
8b	23 700 (1.20)	**1b**	5900 (1.21)	>99	1.46	4.39	4.4
9a	11 500 (1.06)	**7a**	2800 (1.10)	66	1.37	7.82	1.4
9b	13 600 (1.13)	**7b**	3000 (1.06)	80	1.60	5.37	3.0
9c[g]	12 600 (1.06)	**7c**	2700 (1.08)	96	1.70	4.15	5.0

[a]R = Et. [b]Percentage of *Z*-double bond in polymer backbone. [c]Ratio of intensities of Soret band at 406 and 419 nm. [d]EPR peak to trough separation in Gauss. [e]Number of layers of **8** or **9** over which spin is delocalized. [f]Molecular weight of monomer. [g]Reference 17.

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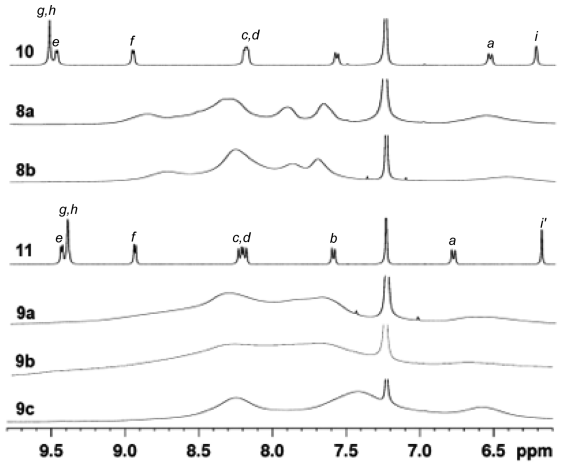

Figure 1. Partial 1H NMR spectra of **10**, **11**, **8a**, **8b**, and **9a**–**c** (400 MHz, $CDCl_3$) at room temperature.

this distance (around 4.5 Å).[22] Accordingly, the mode of interactions between the porphyrin pendants in these polymers would be different due to differences in through-space distance and differences in relative orientation of these pendants.

Absorption Spectra. The Soret band of porphyrin pendants-containing polynorbornenes has been shown to exhibit an exciton splitting, indicating that the adjacent porphyrin pendants in these polymers would be in close proximity.[17] The profiles of the Soret band of substrates containing two interacting porphyrin moieties are very much dependent on the distance and the relative orientation of these chromophores.[30] The absorption spectra for **8** and **9** as well as the corresponding monomers **10** and **11** are shown in Figure 2.

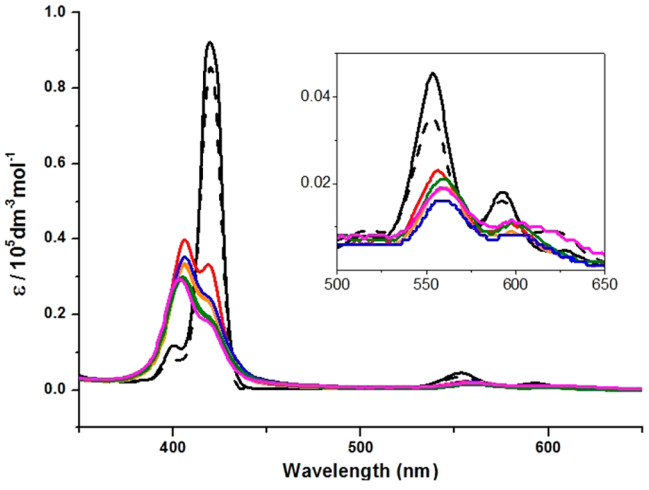

Figure 2. Absorption spectra of **10** (black), **11** (black dash), **8a** (red), **8b** (blue), **9a** (orange), **9b** (green), and **9c** (pink) in CH_2Cl_2 at 25 °C. Inset: expanded region at 500–650 nm.

The Soret band in polymers **8** and **9** appears as two bands due to exciton coupling between adjacent porphyrin chromophores. As shown in Table 1, the relative intensity of the shorter wavelength component (around 406 nm) and the longer wavelength component (around 419 nm) increases from 1.21 to 1.70 as more Z-double bonds are incorporated into the backbone in either **8** or **9**. These results suggest that the mode of interaction between the adjacent porphyrin pendants may be different among these polymers, and the relative orientation of the porphyrin pendants may depend on the stereochemistry of the double bonds on the polymeric backbone. It is known that, when two porphyrin moieties are in eclipsed conformation, the Soret band appears only as a single peak at the shorter wavelength.[30] It seems likely that the orientation of pendants in **8b** and in **9c**, where the double bonds on the polymeric backbones are predominantly *Z*, would orient in a more eclipsed manner and the intensity of the shorter wavelength component would be enhanced. In addition, the relative I_{406}/I_{419} ratios for **9** appear to be slightly higher than those for **8** having similar percentage of *Z*-double bonds, because the spacing occupied by each of the monomeric unit in **8** would be larger than that in **9**.

Electron Paramagnetic Resonance (EPR) Studies. The radical cation of a metalloporphyrin can easily be obtained by oxidation and identified by EPR.[31] The latter technique has extensively been used to study hole hopping in linear- and cyclic-conjugatated porphyrin systems[32,33] as well as multi-porphyrin arrays (in chlorophyll).[34] Electron hopping or delocalization of unpaired electrons among cofacially stacked perylenediimides and related systems leads to narrowing of the EPR signal.[35] It is expected that the nature of delocalization of unpaired electron among cofacially stacked conjugated systems may depend on the relative orientation and the distance of the adjacent π-systems. When such conjugated moieties are appended to a rigid rod polymer, the EPR technique might also be applied to elucidate the stiffness of the polymeric backbone. Thus, monomers **10** and **11** and polymers **8** and **9** were oxidized by $I_2/AgClO_4$[33] to give the corresponding radical cations, whose EPR spectra are shown in Figure 3. It is important to note that the concentrations of all samples in each measurement are kept to have same amount of the porphyrin chromophore. The peak-to-trough separations (ΔH) in these

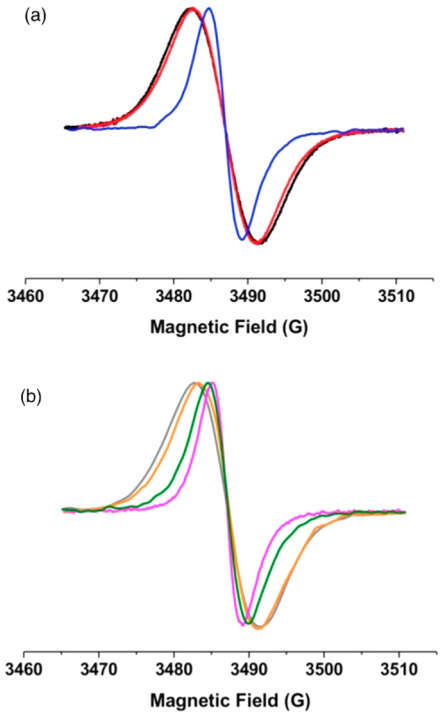

Figure 3. Normalized EPR spectra: (a) $\mathbf{10}^{+\bullet}$ (black), $\mathbf{8a}^{+\bullet}$ (red), and $\mathbf{8b}^{+\bullet}$ (blue); (b) $\mathbf{11}^{+\bullet}$ (gray), $\mathbf{9a}^{+\bullet}$ (orange), $\mathbf{9b}^{+\bullet}$ (green), and $\mathbf{9c}^{+\bullet}$ (pink) in CH_2Cl_2 at 25 °C.

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EPR profiles are also summarized in Table 1. The ΔH values for **8b** enriched with *Z*-double bonds are significantly smaller than that of **8a** mainly with *E*-double bonds. The same trend was observed in $\mathbf{11}^{+\bullet}$ (9.29 G), $\mathbf{9a}^{+\bullet}$ (7.82 G), $\mathbf{9b}^{+\bullet}$ (5.37 G), and $\mathbf{9c}^{+\bullet}$ (4.15 G). These results indicate that the EPR signals become narrower as the % *Z*-double bonds on the polymeric backbones increases. Thus, the effect of polymer conformation may have a significant effect on spin delocalization among the porphyrin pendants. Moreover, the narrowness of the EPR signals appears to be dependent on the distance separating two adjacent chromophores. With similar percentages of *Z*-double bonds, the ΔH values seem to be narrower for **9** than that for **8**.

It has been suggested that the degree of narrowing of the EPR signals would depend on the migration of spin among the cofacially aligned chromophores.[33−36] Using the model for the electron hopping among cofacially stacking chromophores, ΔH_N and ΔH_M, the peak-to-trough separations in the EPR spectra for the polymer and monomer, respectively, are related by eq 3,[33−36] where N_S corresponds to the layers over which the spin is shared on the EPR time scale. These results are summarized in Table 1

$$\Delta H_N = \left(\frac{1}{\sqrt{N_S}}\right)\Delta H_M \tag{3}$$

It is noteworthy that the layers of spin delocalization, N_S, appear to be more prominent when the double bonds in the polymeric backbone are enriched in *Z*-configuration. Thus, the unpaired electron in **9c** can delocalize up to five cofacially aligned porphyrin moieties. Apparently, the mode of spin delocalization may also depend on the relative orientation and distance of the porphyrin pendants. A cartoon representation on the relative orientation of adjacent porphyrin moieties is shown in Figure 4. It seems likely that the more eclipsed

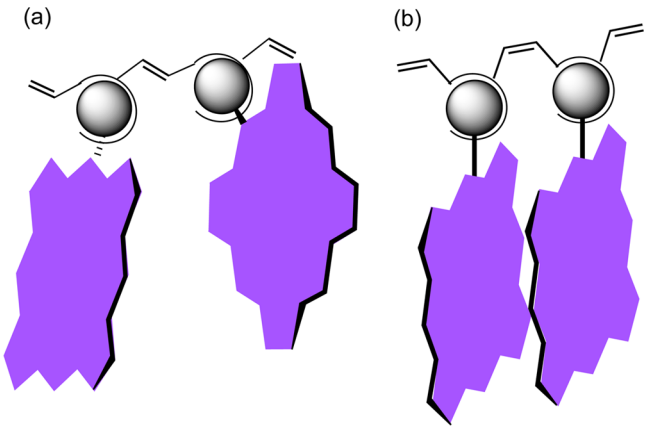

Figure 4. Cartoon representation of the relative orientation of porphyrin pendants with respect to the stereochemistry of double bonds on the polymeric backbone: (a) with trans double bonds and (b) with cis double bonds.

conformation may lead to better delocalization of spin. This trend is parallel to the exciton coupling between the porphyrin pendants as evidenced by the absorption profiles of the Soret band. Interestingly, a plot of ΔH for **9a−c** against the $I4_{06}/I_{419}$ for **9a−c** gives a straight line.[29]

CONCLUSION

In summary, we have demonstrated that the orientations of the pendants in **8** and **9** are closely related to the stiffness of the polymeric backbone, which, in turn, depends on the percentage of *Z*-double bonds. The NMR chemical shifts, the relative intensities of the Soret band absorptions, and the narrowness of the EPR signals are all consistent with this expectation. In other words, we have successfully used these physical techniques to examine the stiffness of polynorbornenes **8** and polycyclobutenes **9** obtained by using ROMP with different catalysts. Our results offer an unprecedented protocol to elucidate the rigidity of the backbones of synthetic polymeric systems. In addition, we have established a useful approach to align an array of chromophores appended onto a rigid polymeric backbone so that the optoelectronic properties can be tuned. On the basis of these findings, design of new systems toward obtaining a better understanding of how the stiffness of polymeric backbone affect photophysical processes for materials applications is in progress.

EXPERIMENTAL SECTION

Instrumentation and Sample Preparation. All air and moisture sensitive reactions were carried out under an atmosphere of dry nitrogen in a glovebox. ^{1}Hand ^{13}C NMR spectra were recorded on a Varian 400 Unity Plus spectrometer, Bruker Advance-500 MHzFT-NMR spectrometer or Bruker AVIII-800 MHz FT-NMR using $CDCl_3$ as solvent at ambient temperature. GPC was performed on a Waters GPC instrument equipped with Waters 1515HPLC pump using Waters 2487 absorbance detector. Polymer (approximately 0.5 mg) in THF (0.1 mL) was filtered through a 0.5-μm filter and 20 μL of the sample was injected into Shodex KF-G, Styragel HR2, Styragel HR3 and Styragel HR4 column (7.8 × 300 mm) with oven temperature at 40 °C using standard polystyrene samples (1.84×10^5 to 996 Da) for calibration. THF was used as eluent (flow rate 1.0 mLmin^{-1}). Waters Empower HPLC/GPC network software was used for data analyses. *E*-Isotactic polynorbornene **8a** and *Z*-isotactic polycyclobutene **9c** were prepared according to reported procedures.[17,22]

Polynorbornene (8b). Under N_2 atmosphere in a drybox, a solution of **10** (70 mg, 0.06 mmol) in CH_2Cl_2 (3 mL) was treated with a solution of **4** (3 mg, 3.9×10^{-3} mmol, 7 mol %) in CH_2Cl_2 (0.5 mL). The reaction mixture was stirred for 10 min at rt, after which, benzaldehyde (300 μL, 2.0 mmol) was added and the mixture was stirred for an additional 1 h. The mixture was added dropwise to vigorously stirring EtOAc (30 mL) affording a fine solid, which was collected, washed with MeOH and evacuated under reduced pressure to afford **8b** as a purple solid (63 mg, 90%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.70−1.50 (br, 59 H), 1.50−4.70 (br, 20 H), 4.70−5.80 (br, 2 H), 6.00−7.00 (br, 2 H), 7.60−9.50 (br, 14 H. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.1, 22.7, 29.4, 29.7, 30.6, 31.9, 34.2, 35.8, 38.7, 47.7, 49.2, 111.5, 116.6, 117.2, 118.4, 119.8, 127.4, 132.2, 135.9, 139.8, 147.9, 150.7, 165.6. GPC: M_n = 23700; PDI = 1.20.

Polycyclobutene (9a). Under N_2 atomosphere, a solution of **11** (70 mg, 0.06 mmol) in CH_2Cl_2 (3 mL) was treated with a solution of **3** (5 mg, 6.2×10^{-3} mmol, 10 mol %) in CH_2Cl_2 (0.5 mL). The reaction mixture was stirred for 1 h at room temperature, after which ethyl vinyl ether (0.5 mL) was added and the mixture was stirred for 20 min. The mixture was concentrated, and the residual solution was added to EtOAc (30 mL). Precipitate was collected, rinsed with EtOAc and evacuated under reduced pressure to afford polymer **9a** as purple solid (67 mg, 95%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.70−1.50 (br, 57 H), 1.60−5.00 (br, 18 H), 5.00−5.90 (br, 2 H), 6.10−6.90 (br, 2 H), 7.40−9.50 (br, 14 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.1, 22.7, 29.7, 31.9, 35.8, 38.6, 45.5, 52.7, 110.9, 117.1, 119.8, 127.4, 130.7, 132.4, 135.3, 139.8, 147.9, 150.7, 165.5. GPC: M_n = 11500; PDI = 1.06.

Polycyclobutene (9b). Under N_2 atomosphere, a solution of **11** (70 mg, 0.06 mmol) in CH_2Cl_2 (5 mL) was treated with a solution of

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5 (3.2 mg, 4.1 × 10^{-3} mmol, 7 mol %) in CH_2Cl_2 (0.5 mL). The reaction mixture was stirred for 20 min at room temperature, after which benzaldehyde (300 μL, 2.0 mmol) was added and the mixture was stirred for an additional 1 h. The mixture was added dropwise to vigorously stirring EtOAc (30 mL), affording a fine solid. The solid was collected, washed MeOH and evacuated in vacuo to afford **9b** as purple solid (65 mg, 93%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.70−1.80 (br, 57 H), 1.80−5.40 (br, 18 H), 5.45−6.10 (br, 2 H), 6.30−6.90 (br, 2 H), 7.40−10.25 (br, 14 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.1, 22.7, 29.7, 31.9, 34.3, 35.8, 38.7, 45.7, 51.4, 52.2, 110.9, 119.8, 127.4, 130.1, 132.5, 135.4, 139.7, 148.0, 150.6, 165.5. GPC: M_n = 13600; PDI = 1.13.

Ethanolysis of 8a. Under N_2 atmosphere, a solution of **8a** (55 mg, 0.04 mmol) in $CHCl_3$ (20 mL) was added to NaOEt (96 mg, 1.4 mmol) in EtOH (4 mL) at 0 °C. After stirring at rt for 24 h, the mixture was poured into water (40 mL) and extracted with $CHCl_3$ (30 mL x 2). The combined organic layer was washed with brine (20 mL) and dried ($MgSO_4$). The solvent was removed in vacuo to give a residue that was taken into $CHCl_3$ (1 mL) and then added to Et_2O (20 mL). Precipitate was collected, rinsed with Et_2O and evacuated under reduced pressure to afford **1a** as a white powder (11 mg, 85%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.22−1.41 (br, 3 H), 1.48−1.70 (br, 1 H), 1.71−1.97 (br, 1 H), 2.61−3.40 (br, 8 H), 4.16−4.43 (br, 2 H), 5.18−5.55 (br, 2 H), 6.34−6.63 (br, 2 H), 7.74−8.10 (br, 2 H). ^{13}C NMR (CDCl3, 100 MHz): δ 14.4, 35.7, 36.1, 37.5, 39,9, 44.5, 46.4, 49.5, 60.1, 111.5, 117.5, 131.2, 131.7, 150.7, 166.9. GPC: M_n = 3700; PDI = 1.15. The ratio of *E*/*Z* double bonds (82/18) was determined by integrating the relative intensities at δ 35.7 and 36.1 against 39.9 using inverse gated decoupling technique on a Bruker AVIII-800 MHz FT-NMR spectrometer.

Ethanolysis of 8b. In a manner similar to that described above for the ethanolysis of **8a**, reaction of **8b** (55 mg, 0.2 mmol) and NaOEt (96 mg, 1.4 mmol) (96 mg, 1.4 mmol) yielded **1b** as a white solid ((10 mg, 82%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.18−1.50 (br, 4 H), 1.80−2.05 (br, 1H), 2.65−3.55 (br, 8 H), 4.16−4.46 (br, 2 H), 5.15−5.45 (br, 2 H), 6.34−6.64 (br, 2 H), 7.75−8.10 (br, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.5, 38.9, 40.8, 47.5, 49.4, 60.2, 111.4, 117.9, 131.3, 132.3, 150.5, 166.8. GPC: M_n = 5900. PDI = 1.21.

Ethanolysis of 9a. In a manner similar to that described above for the ethanolysis of **8a**, reaction of **9a** (55 mg, 0.2 mmol) and NaOEt (96 mg, 1.4 mmol) (96 mg, 1.4 mmol) yielded **7a** as a white solid (10 mg, 90%): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.20−1.45 (br, 3 H), 2.60−3.75 (br, 6 H), 4.10−4.55 (br, 2 H), 5.15−5.85 (br, 2 H), 6.18−6.65 (br, 2 H), 7.65−8.15 (br, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.4, 40.8, 45.6, 52.6, 60.2, 110.5, 129.8, 131.4, 150.2, 166.8. GPC: M_n = 2800; PDI = 1.10. Using same NMR technique as described for the ethanolysis of **8a**, the ratio of *E*/*Z* double bonds (34/66) was determined by integrating the relative intensities at δ 45.6 against 40.8.

Ethanolysis of 9b. In a manner similar to that described above for the ethanolysis of **8a**, reaction of **9b** (55 mg, 0.2 mmol) and NaOEt (96 mg, 1.4 mmol) yielded **7b** as a white solid (9 mg, 86%). ^{1}H NMR ($CDCl_3$, 800 MHz): δ 1.20−1.45 (br, 3 H), 2.60−3.80 (br, 6 H), 4.00−4.50 (br, 2 H), 5.00−5.80 (br, 2 H), 6.15−6.65 (br, 2 H), 7.65−8.00 (br, 2 H). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 14.4, 40.7, 45.5, 52.8, 60.2, 110.5, 117.8, 129.8, 131.4, 150.2, 166.8. GPC: M_n = 3000; PDI = 1.06. The ratio *E*/*Z* double bonds is 20/80 using the same technique as described above.

Determination of Stereochemistry of Double Bonds in 1 and 7. *E*/*Z* double bonds ratio was determined according to the integration of ^{13}C NMR spectra recorded on an 800 or 500 MHz NMR machine for carbon with inverse gate proton decoupling during acquisition. About 8000 scans were collected for the spectrum using 30° pulse, a relaxation delay of 7 s and an inverse gate decoupled pulse sequence to ensure the quantitative information were used. Exponential multiplication of line broadness = 5 was applied prior to the Fourier transformation. The NMR spectra of ethanolysis polymers are shown in Figures S7−S10.

EPR Measurements. EPR spectra were acquired at the X band (9.5 GHz) by using EMX spectrometer (Bruker Biospin) equipped with a Bruker TE102 cavity at room temperature. Typical parameters for EPR measurements are as follows: microwave frequency 9.7 GHz, microwave power 2 mW, modulation frequency 100 kHz, modulation amplitude 0.1 or 1.0 mT, and receiver gain 6.32 × 10^3. A solution of **10**, **11**, **8**, or **9** (10 mg/mL) were generated by addition of a 20 μL solution of I_2 and $AgClO_4$ (2 m) in acetonitrile. This solution was subject to EPR measurements.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR and HMQC spectra and GPC results of all polymers and a scheme showing ethanolysis of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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N.-T.L. and K.S. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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(36) One reviewer questioned if "EPR spectra could also be affected by the polarity of the environment and difference in diffusion behavior of the polymer". The charge delocalization is reflected by the broadness of EPR signals due to intrachain phenomenon. Since the concentrations for the chromophores in each of the polymeric samples were kept to be same in all of these studies in the same DCM solvent, the polarity of the medium and the mass issues could be eliminated.