# Soluble Polyacetylene Derivatives by Chain-Growth Polymerization of Dienes

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S *Supporting Information*

ABSTRACT: A new method for the fabrication of soluble polyacetylene derivatives was developed based on bromination—dehydrobromination of bicyclic diene polymers. High molecular weight polymer precursors were synthesized by radical 1,4-polymerization of the corresponding dienes, which contained a bicyclo[2.2.2]octane skeleton. Polymer precursors with narrow molecular distributions were prepared by nitroxide-mediated polymerization of the bicyclic diene monomers. Regioselective elimination from the brominated polymer afforded a polyacetylene derivative contaning bicyclic substituents, which was readily soluble in common organic solvents. The polymer electronic bandgap, obtained by optical and electrochemical measurements, was in the range 1.4—1.7 eV. Low bandgap values were attributed to the conformational inflexibility of the bicyclic substituent forcing coplanar orientation of the backbone double bonds. Solid-state conductivity of the produced polymer in the undoped form was measured to be 1.5×10^{-5} S/m. This new synthetic method allows for the chain-growth production of polyacetylene derivatives that possess favorable electronic properties and superior solubility characteristics to pristine polyacetylene.
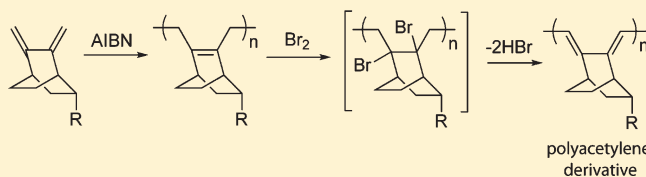
INTRODUCTION

Polymers with π-conjugated backbones have been a subject of intensive research for use in electronic devices, including light-emitting diodes,[1,2] solid-state lasers,[3] field-effect transistors[4,5] and photovoltaics,[6,7] as well as in sensors,[8,9] actuators,[10] and corrosion-resistant coatings.[11] Controlling multiple factors affecting the performance of conjugated polymers, such as the electronic bandgap, charge-carrier mobility, and environmental stability, is an ongoing challenge in this field. Each application puts its own stringent demands on the performance of conjugated macromolecules, and scientists are striving to address these challenges by manipulating the intrinsic chemical structure and the aggregation behavior of the conjugated polymer chains. A vital part of this multidisciplinary effort is the preparation of tailored semiconducting polymeric materials and understanding their complex structure—property relationships. Currently, most conjugated polymers are synthesized via step-growth polymerization protocols, often involving metal-mediated aryl couplings.[12] Fundamental limitations of the step polymerization kinetics[13] significantly limit the attainable molecular weights of the conjugated polymers and also prohibit the use of controlled polymerizations to produce well-defined conjugated polymers or block copolymers. There is an increasing interest in developing new synthetic methods to generate conjugated polymers via controlled chain-growth polymerization mechanisms, which will allow for a superior chain length control and the synthesis of complex nanostructured systems.

Recently, there has been tremendous progress in developing chain-growth polymerization strategies for the preparation of conjugated polyaromatics.[14—18]

Polyacetylene (PA) is the simplest conjugated polymer with a linear polyene backbone structure. Since its initial discovery, PA has been a subject of intensive research due to its unique structure and extremely high conductivities in the doped form.[19—21] However, the processing of PA is hindered by its poor solubility in organic solvents. There are two distinct approaches that can be used to circumvent this limitation and improve the processability of PA. The first approach takes advantage of soluble polyacetylene precursors that can be converted to PA post processing.[22—25] The second approach uses PA derivatives with regularly spaced substituents to improve solubility characteristics of PA.[26—28] The latter method can also be used to alter or fine-tune the electronic properties of polyacetylene.

There are two general strategies that have been successfully utilized for the preparation of substituted polyacetylene derivatives via a chain-growth polymerization mechanism: metal-catalyzed alkyne polymerization[28—30] and ring-opening metathesis polymerization (ROMP) of cyclooctatetraenes.[31—35] The outcome of these two methods is different in the relative

Scheme 1

Scheme 2
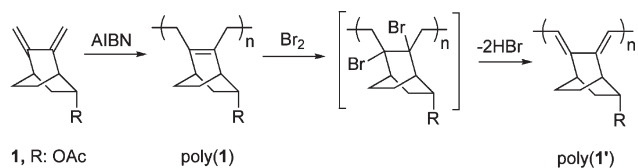
positions of the substituents, which has a dramatic effect on the polymer properties. The direct alkyne polymerization method provides PA substituted at every second carbon. These polymers have excellent solubility characteristics, but having substituents so close to each other results in twisted backbone conformations, which leads to bandgaps much larger than pristine PA.[29] On the other hand, the ROMP method generates polyacetylene derivatives with a substituent at every eighth carbon. Such PA derivatives have electronic properties very close to pristine PA, but their solubilities are only marginally better than polyacetylene itself.[34]

In this contribution, we report a new chain-growth polymerization strategy to synthesize PA derivatives with bicyclic substituents. We demonstrate that polymer precursors prepared from bicyclic dienes can be converted to soluble polyacetylene derivatives by bromination—dehydrobromination sequence in an efficient manner. The bicyclic substituents not only improve the solubilities of the produced PA derivatives but also force the coplanar orientation of the backbone, resulting in favorable electronic properties.

■ RESULTS AND DISCUSSION

Synthetic Strategy. The new approach to the synthesis of polyacetylene derivatives is illustrated in Scheme 1. A bicyclic diene monomer is polymerized in a 1,4-addition mode to produce the corresponding polydiene polymers. We have shown previously that similar dienes polymerize predominantly (>95%) by 1,4-addition under free-radical polymerization conditions.[36] Backbone unsaturations in the polymer are then brominated by a bromine addition reaction. Finally, dehydrobromination reaction introduces double bonds in the backbone and converts it to a fully conjugated structure. A unique aspect of this elimination reaction is that it is completely regioselective: only methylene protons in the backbone can be eliminated with the corresponding bromide, while the bridgehead CH cannot participate in the reaction due to violation of the Bredt's rule. Such regioselectivity cannot be achieved by using traditional polydienes, such as polybutadiene or polyisoprene, or even during HCl elimination from poly(vinyl chloride), another strategy employed for the synthesis of a conjugated polyene structure.[37] The bromination—dehydrobromination sequence can proceed in an efficient manner and has been used before to prepare conjugated polymers, for example, from poly(cyclopentadiene).[38] However, in this case, polymers with a multitude of defects and isomeric repeat units were produced due to the presence of multiple elimination sites.

Another advantage of our synthetic strategy is that free-radical polymerization, utilized for the synthesis of polydiene precursors, can produce high molecular weight polymers and can be adapted to proceed in a controlled/living fashion, thus allowing for the
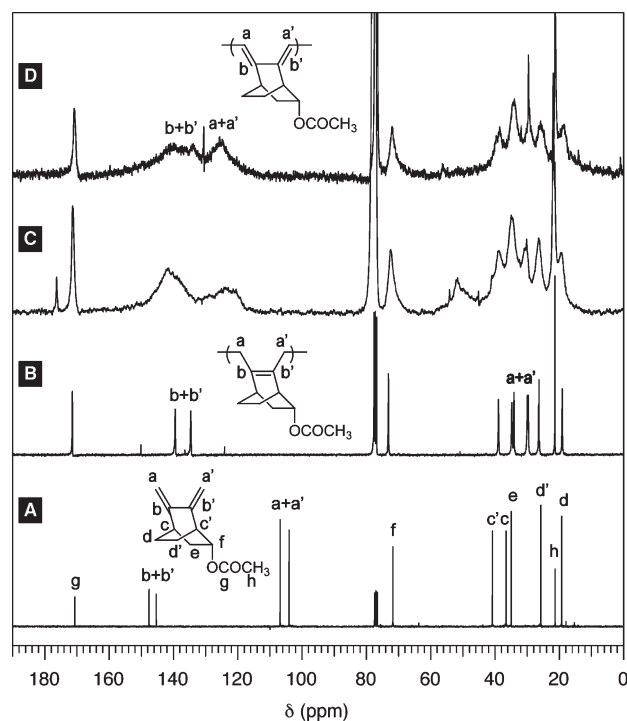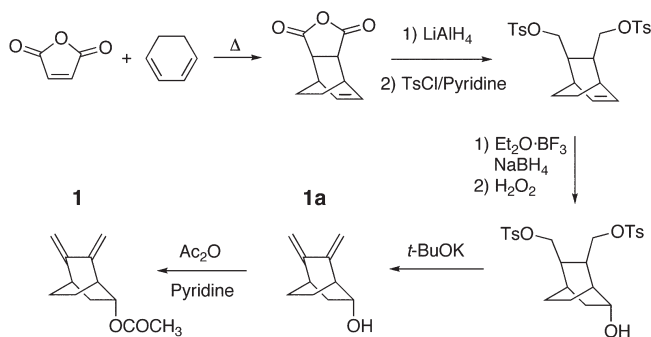
Figure 1. ^{13}C NMR spectra of monomer **1** (A), poly(**1**) (B), and poly(**1'**) before (C) and after (D) thermal treatment at 150 °C.

fabrication of well-defined polyacetylene derivatives with controlled molecular weights and low polydispersities.

Monomer Synthesis. Bicyclic diene monomers were synthesized according to a literature procedure (Scheme 2).[39] Diels—Alder reaction between maleic anhydride and cyclohexadiene produced the bicyclic skeleton in high yields. The anhydride group was converted to a diol by LiAlH$_4$-mediated reduction and subsequently esterified by reacting with p-toluenesulfonyl chloride. The hydroboration—oxidation sequence was then used for indirect hydration of the double bond. The diene structure was obtained by elimination of p-toluenesulfonic acid in the presence of potassium $tert$-butoxide. Finally, the hydroxy substituent was acetylated to produce monomer **1** (Figure 1A).

Polyacetylene Synthesis. The bicyclic diene **1** as well as the hydroxy-substituted derivative **1a** and the unsubstituted diene (2,3-bis(methylene)bicyclo[2.2.2]octane) were all successfully

polymerized under free-radical polymerization conditions. Semicrystalline polymer produced from the unsubstituted diene was only soluble in organic solvents at high temperatures, while the polymer produced from the OH-substituted diene **1a** was only soluble in polar solvents, such as DMF and DMSO. Therefore, we chose to work with poly(**1**), which exhibited good solubility characteristics in most organic solvents.

Polymerization of monomer **1** in toluene provided a white powdery polymer after precipitation in methanol. Even without optimization, polymers with molecular weights as high as 33 kg/mol (relative to polystyrene calibration) could be obtained. This is not surprising given the fast polymerization kinetics that we previously reported for similar bicyclic diene monomers.[36] Nitroxide-mediated polymerization, one of the few methods to achieve controlled synthesis of polydienes,[40,41] was used to prepare poly(**1**) with narrow molecular weight distributions. Thus, in the presence of a nitroxide radical, 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide, and benzoyl peroxide, poly(**1**) with a polydispersity index as low as 1.20 was obtained.

^{1}H and ^{13}C NMR spectra of poly(**1**) exhibited well-resolved signals that were consistent with the expected polymer structure. In the ^{1}H NMR spectrum of poly(**1**), no signals in the olefinic region were detected, indicating that the polymerization proceeded predominantly (>95%) by 1,4-addition (Figure S1, Supporting Information). In the ^{13}C NMR spectrum, two signals at 136 and 140 ppm were assigned to the olefinic carbons in the backbone (Figure 1B). The backbone methylene carbon signals moved from 104 and 107 ppm to 30 ppm after polymerization (Figure 1A,B). The remaining signals of the bicyclic group and the acetate substituent in the polymer were in close agreement to the corresponding signals in the monomer, indicating that no rearrangements or other major side reactions were taking place during polymerization. Since the acetoxy substituent was so far away from the backbone, it was impossible to deduce stereoregularity of the polymer from NMR analysis. Poly(**1**) had a glass transition temperature of 78 °C, as measured by differential scanning calorimetry (DSC, Figure S2 in the Supporting Information). Despite the presence of bulky bicyclic substituents, two methylene groups in the backbone afforded enough flexibility for the polymer to exhibit a relatively low T_g.

Bromination of the backbone unsaturations in poly(**1**) was achieved by a simple bromine addition. When an equimolar amount of bromine was used, the completion of the reaction was evident by the disappearance of yellow/brownish color to form a colorless solution, suggesting a complete consumption of bromine. After a short delay (~5 min), spontaneous dehydrobromination commenced, changing the color of the solution to darker brown and ultimately black. When a slight excess of bromine was used, no spontaneous dehydrobromination was observed, presumably due to the slightly acidic nature of the remaining solution. Subsequently, when aqueous sodium bisulfite was added to remove the excess bromine, the solution color slowly turned black, suggesting that dehydrobromination was taking place. Upon completion of transformations, the polymer was recovered as a black powder by precipitation from methanol. The produced polymer was readily soluble in common organic solvents, such as tetrahydrofuran, chloroform, and toluene. We hypothesize that dehydrobromination is driven by the formation of the conjugated backbone, which is also responsible for the dark color of the forming polymer. Similar behavior has been observed during the synthesis of conjugated polymers by bromination–dehydrobromination of polycyclopentadiene.[38]
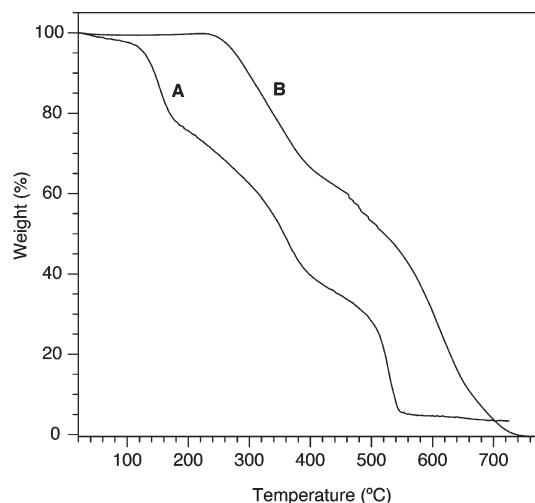

Figure 2. Thermogravimetric analysis of poly(**1**′) as prepared (A) and after thermotreatment at 150 °C (B).

Scheme 3
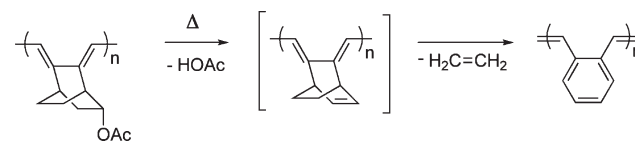
NMR spectra of the newly formed polymer (poly(**1**′)) exhibited broad signals, suggesting the formation of a rigid structure. This was also corroborated by DSC analysis, where poly(**1**′) did not exhibit any thermal transitions (glass transition or melting) up to 200 °C (Figure S2, Supporting Information). In the ^{1}H NMR spectrum, a new peak at 6.8 ppm was observed, which was attributed to the backbone C*H* protons. The broadness of the peaks and the overlap with other signals prohibited any quantitative analysis. In the ^{13}C NMR spectrum, while significantly broadened, the peaks were well-resolved and provided additional evidence for the formation of an unsaturated backbone. A new signal at 125 ppm in the olefinic region was attributed to the CH carbon in the backbone (Figure 1C). DEPT analysis (Figure S3, Supporting Information) confirmed that the signal at 125 ppm was originating from a CH carbon, while the signal centered around 140 ppm was coming from a quaternary carbon, thus accounting for all carbons of the conjugated backbone repeat unit. A new peak at 50 ppm was also observed. We assigned this signal to the carbon attached to a bromine atom, a structural fragment remaining after incomplete dehydrobromination. Thermogravimetric analysis (TGA) of the polymer showed a marked weight loss at 140 °C, corresponding to about 20 wt % (Figure 2A), which was attributed to the elimination of the remaining HBr from the sample. Thus, dehydrobromination was facilitated by thermal treatment at 150 °C, after which the polymer exhibited improved thermal stability up to 270 °C (Figure 2B). In the ^{13}C NMR spectrum of the thermally treated polymer, the signal at 50 ppm was significantly diminished (Figure 1D). Elemental analysis indicated that there were only 1.1 mol % bromine atoms left in the sample after thermal treatment, some of which may be originating from brominated 1,2-addition repeat units.
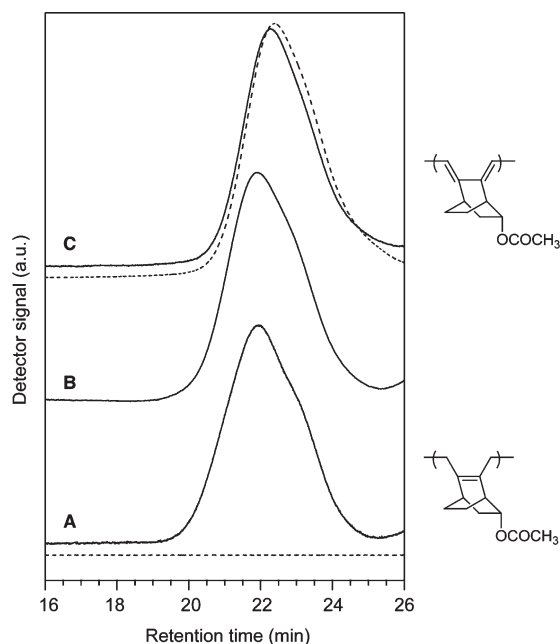
Figure 3. GPC traces of poly(**1**) (A) and poly(**1′**) before (B) and after (C) thermotreatment: RI detector (solid lines), UV–vis detector at 600 nm (dashed lines).
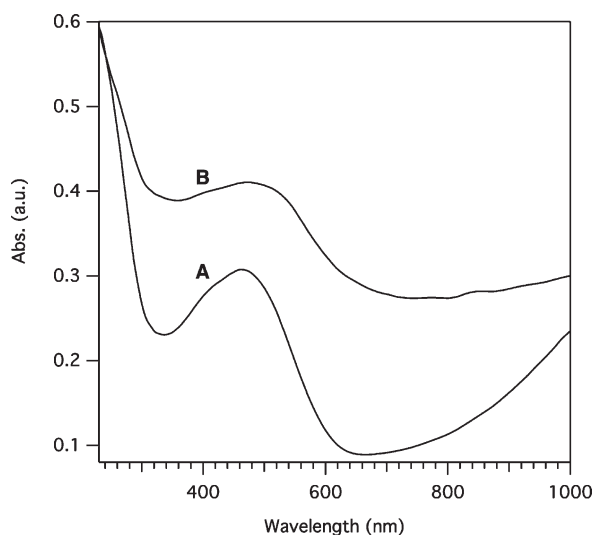
Figure 4. UV–vis spectra of poly(**1′**) in a chloroform solution (A) and as a thin film (B).

It must be noted that thermal degradation of poly(**1′**) proceeded in two steps, where the first step commenced at 270 °C and led to about 45% weight loss (Figure 2). We propose that this decrease in weight corresponds to the elimination of acetic acid and subsequent retro-Diels–Alder reaction,[36] forming poly(*o*-phenylenevinylene) (Scheme 3). These transformations should lead to about 50% weight loss, which is in agreement with the observed TGA results.

Molecular weight characterization of the polymers by GPC post bromination–dehydrobromination and thermal treatment revealed that there were no major side reactions, such as cross-linking or polymer chain degradation, during these transformations (Figure 3). The shape and the elution time of the GPC
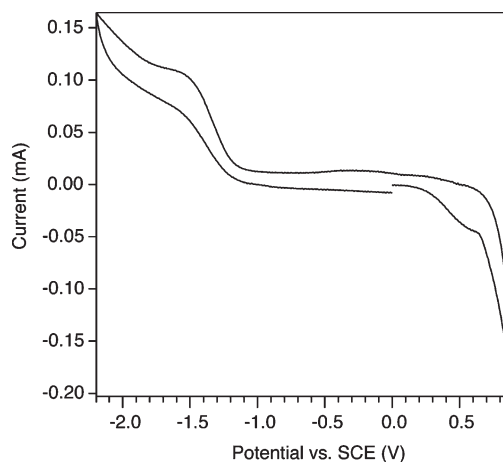
Figure 5. Cyclic voltammogram (20 mV/s) of poly(**1′**) on a platinum electrode in CH$_3$CN (0.1 M Bu$_4$NPF$_6$).

peaks remained mostly unchanged after backbone modifications. When a UV detector (set to detect at 600 nm) was used, no signal was observed for poly(**1**), while the conjugated poly(**1′**) showed a GPC trace matching the one observed by the refractive index detector. The results suggest that the color of the polymer sample is originating from the polymer itself and not from small molecular weight impurities in the sample.

The presence of the bicyclo[2.2.2]octane skeleton in poly(**1**) was crucial for the successful outcome of backbone transformations. When polymers containing a norbornane substituent were used, such as those prepared from 2,3-dimethylenenorbornane,[36] bromination led to complete polymer degradation, as evidenced by GPC and NMR analyses. This might be a result of the susceptibility of norbornyl cations to undergo rearrangements[42] leading to undesired transformations. Therefore, the bicyclo[2.2.2]octane substituent not only provided directionality for clean dehydrobromination but also afforded stability necessary to complete the transformations with a minimum amount of side reactions.

Electronic Properties. The UV–vis spectrum of the prepared polyacetylene derivative dissolved in chloroform showed a strong absorption band with a maximum at 460 nm (Figure 4A), indicating the presence of an extended conjugation. There was also a significant band appearing in the near-IR region. Such a band is often observed in polyacetylene films doped to semiconductor levels.[43−45] It is not clear whether this band is indicative of doping in our case as well. No metal catalyst, which can cause adventitious doping, was used during either polymerization or backbone modification reactions. Bromine (which can act as a dopant) was removed by reaction with sodium bisulfite before the formation of a conjugated polymer structure. In addition, the polymer sample was thermotreated at 150 °C prior to UV–vis analysis and was handled with minimal exposure to air. When deposited as a film, the polymer exhibited an absorption maximum of 480 nm with a tail stretching beyond 700 nm, while no near-IR band was observed (Figure 4B). The bandgap measured from the optical absorption edge was 1.7 eV. A slight red shift in the absorption maximum when going from solution to film suggests reorganization of polymer chains in the solid state. Prolonged exposure to air deteriorated the conjugated polymer structure, as evidenced by disappearance of absorption bands from the UV–vis spectrum.

Cyclic voltammetry (CV) analysis of the synthesized poly-acetylene derivative revealed a presence of broad oxidation and reduction waves, consistent with an electroactive organic structure (Figure 5). The electrochemical bandgap was found to be 1.4 eV, calculated based on the onset of oxidation at 0.25 V and the onset of reduction at −1.15 V. The obtained bandgaps are considerably lower than those reported for other polyacetylene derivatives with substituents at every second carbon.[46,47] In fact, the bandgap measured for poly($1'$) is surprisingly close to that of a pristine polyacetylene.[21,43] Larger bandgaps of substituted polyacetylene derivatives have often been attributed to the steric repulsion between the substituents resulting in a conformational twist of the backbone.[29] We hypothesize that a low bandgap of poly($1'$) is a result of conformational inflexibility of the bicyclic substituent, which forces coplanar orientation between backbone unsaturations. A similar effect has been observed during polymerizations of bicyclic dienes, where high polymerization rates have been attributed to coplanar orientation of the double bonds in the monomer.[36] It appears that the bicyclic substituent allows for markedly improved solubility, and thus processability, of polyacetylene, while preserving its desirable electronic properties.

The conductivity of poly($1'$) was obtained by measuring current as a function of applied electric field on a metal−polymer−metal structure (Figure S4, Supporting Information). The undoped polymer sample used for conductivity studies was thermotreated at 150 °C and was handled under air-free conditions during synthesis, processing, and measurements. An interdigitated metal−polymer−metal device was fabricated and measured to obtain current values corresponding to applied electric fields across the device. To calculate the conductivity of the polymer film, an effective device area of 4.2×10^{-12} m^2 was used to obtain the current density. Then, the conductivity was calculated using the equation $J = \sigma E$, where J is the current density, σ is the conductivity, and E is the electric field. The conductivity of poly($1'$) obtained from the slope of the linear fit between the electric field and the current density was 1.5×10^{-5} S/m. The obtained conductivity value is consistent with those of other undoped conjugated polymers,[48] suggesting that bicyclic substituents do not have a detrimental impact on charge transport in the solid state. Detailed characterization of the electronic properties of poly($1'$) is under way in our laboratories.

■ EXPERIMENTAL SECTION

Materials. Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol; all other commercially available reagents and solvents were used without purification. Monomer **1a**[39] and 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide[40] were prepared according to literature procedures.

Synthesis of 1. Monomer **1a** (0.7 g) was dissolved in a mixture of pyridine (3 mL) and acetic anhydride (2.4 mL) and stirred at room temperature overnight. Afterward, the reaction mixture was poured into ice water and extracted with dichloromethane (3 × 10 mL). The organic layer was dried over MgSO$_4$, and the solvent was evaporated. The residue was purified by flash chromatography (hexanes/ethyl acetate = 10:3, R_f = 0.48) to obtain monomer **1** (0.82 g, 82% yield). ^{1}H NMR (CDCl$_3$): δ 5.40 (s, 1H), 5.28 (s, 1H), 4.92 (s, 1H), 4.90 (s, 1H), 4.77 (s, 1H), 2.61 (s, 1H), 2.42 (s, 1H), 1.98−2.13 (m, 5H), 1.77 (m, 1H), 1.54 (m, 1H), 1.51 (m, 1H), 1.27 (m, 1H). ^{13}C NMR (CDCl$_3$): δ 170.64, 147.59, 145.35, 109.98, 104.03, 71.74, 40.79, 36.56, 34.95, 25.53, 21.31, 19.27.

Nitroxide-Mediated Polymerization of 1. Monomer **1** (100 mg, 0.52 mmol), 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide

(1.2 mg, 5.4 μmol), and benzoyl peroxide (0.4 mg, 1.6 μmol) were dissolved in toluene (0.1 mL), and the mixture was degassed by three freeze−pump−thaw cycles, sealed under nitrogen, and placed in an oil bath at 100 °C. After 120 h, the contents were diluted with dichloromethane and precipitated in methanol. The polymer was filtered and dried in a vacuum oven overnight. Yield = 65 mg. GPC (polystyrene standards): M_n = 12.5 kg/mol, M_w/M_n = 1.20.

Radical Polymerization of 1. A mixture of **1** (0.2 g), AIBN (2 mg), and 0.2 mL of toluene was degassed by three freeze−pump−thaw cycles, sealed under nitrogen, and placed in an oil bath at 65 °C. After 12 h, the contents were diluted with dichloromethane and precipitated in methanol. The polymer was filtered and dried in a vacuum oven overnight. Yield = 0.15 g. GPC (polystyrene standards): M_n = 32.7 kg/mol, M_w/M_n = 2.45.

Bromination−Dehydrobromination. Bromine (1.5 mmol) in 5 mL of dichloromethane was added dropwise to poly(**1**) (1 mmol) dissolved in 5 mL of dichloromethane. After stirring for an additional hour, 5 mL of 1 M NaHSO$_3$(aq) was added to the reaction mixture. The organic layer became colorless first and then got darker with time, eventually turning dark brown. After 1 h, the organic phase was separated and the solvent was evaporated. The residue was diluted with dichloromethane and precipitated in methanol three times. Subsequently, the dried polymer was thermally treated at 150 °C for 16 h in a vacuum oven.

Conductivity Measurements. A metal semiconductor metal (MSM) structure was used to measure the conductivity of poly($1'$). A glass substrate was cleaned using acetone, methanol, and deionized water. For submicrometer patterning, a primer and a photoresist (Shipley 1818) were spin-coated on the glass substrate at 5000 rpm for 30 s. Then, it was baked on the hot plate at 120 °C for 90 s. The substrate was exposed under UV by using a photomask and a mask aligner (Karl Suss MJB3) for 10 s and developed by using MF319 developer for 45 s. Subsequently, metal deposition was performed by using an electron beam evaporator. A titanium layer (10 nm) for good adhesion and a gold layer (50 nm) were deposited at a deposition rate of 1 Å/s under 5×10^{-8} Torr. Finally, the patterned electrodes were obtained after a lift-off process. The resulting metal electrodes have an interdigitated structure to increase the effective device area, with a 4 or 5 μm gap. The device was diced to a smaller piece in order to fit into a ceramic lead chip carrier. The device was fixed in the chip carrier and two electrodes were connected to the leads using a standard wire bonding process. This prepared device structure was then placed into a nitrogen purged glovebox system and poly($1'$) (2 wt %) in a 1,2-dichlorobenzene solution was spin-coated on the device surface at 1800 rpm for 30 s. The final metal−polymer−metal device was dried using a hot plate at 80 °C for 10 min. The prepared sample was kept in a sealed box with a feed through to prevent any oxygen exposure that causes device degradation. The conductivity measurement was performed using a computer-controlled source meter (Keithley 2400) by applying an electric field (sweeping from 0 to 200 kV/cm) across the two electrodes with a 4 μm gap.

Measurements. NMR measurements were performed on a Varian Inova-500 (500 MHz) spectrometer by using CDCl$_3$ as a solvent. Gel permeation chromatography (GPC) analysis was carried out on Viscotek's GPCMax with three Olexis columns (Polymer Laboratories, Varian Inc.) and TDA302 tetradetector array system, which contained a refractive index, UV, viscosity, and low (7°) and right angle light scattering modules. Tetrahydrofuran was used as a carrier solvent at 30 °C. The system was calibrated with 10 linear polystyrene standards from 1.2×10^6 to 500 g/mol. UV−vis spectra were recorded on Agilent 8453 at room temperature by using dichloromethane as a solvent. Thermogravimetric analysis was performed on a Perkin-Elmer TGA7 under nitrogen flow at a heating rate of 10 °C/min.

Cyclic voltammetry was carried out in a three-electrode compartment cell with a volume of electrolyte solution (0.1 M Bu$_4$NPF$_6$ in acetonitrile),

using the saturated calomel electrode (SCE) as reference, a platinum wire as counter electrode, and a platinum disk (effective area 0.5 cm^2) as a working electrode, on which a thin polymer film was produced by dip-coating. The experiment was performed using a Model 263A potentiostat—galvanostat (EG&G Princeton Applied Research) under a nitrogen atmosphere.

■ CONCLUSIONS

We developed a novel strategy for the synthesis of polyacetylene derivatives by using radical polymerization of bicyclic dienes and subsequent polymer transformations. The polymer precursor was synthesized via 1,4-polymerization of monomer **1**. High molecular weight polymers were obtained by a traditional radical polymerization, while a nitroxide-mediated polymerization of **1** afforded polymers with narrow molecular weight distributions. The conjugated polymer was synthesized by bromination/dehydrobromination of poly(**1**). The presence of a bicyclic substituent allowed for regioselective elimination to produce a well-defined conjugated backbone. The obtained polyacetylene derivative was soluble in common organic solvents. The bandgap of poly(**1'**) was obtained by optical and electrochemical measurements to be in the range 1.4—1.7 eV, which was notably lower than bandgaps reported for polyacetylene derivatives with substituents on every second carbon. We hypothesize that conformational inflexibility of the bicyclic substituent was responsible for the coplanar orientation of backbone double bonds, thus leading to lower bandgaps. The conductivity of undoped poly(**1'**) in the solid sate was measured to be 1.5×10^{-5} S/m. The described methodology allows for the preparation of polyacetylene derivatives with favorable electronic properties and superior solubility characteristics than pristine polyacetylene.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** ^{1}H NMR, ^{13}C NMR, DSC, and conductivity characterization data for the synthesized polymers (Figures S1—S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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