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Preparation and Characterization of Conjugated Polymers Made by Postpolymerization Reactions of Alternating Polyketones

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S Supporting Information

ABSTRACT: Conjugated polymers possessing a poly(2,5-dimethylene-2,5-dihydrofuran) backbone were prepared through postpolymerization reaction of styrenic polyketones with bromine in one-pot reactions. The modification is proposed to proceed via condensation of two repeating units to form a fully characterized polymer with a poly(2,5-dimethylenetetrahydrofuran) backbone. Subsequent bromination and elimination of HBr yield a polymer with a fully conjugated carbon backbone. The new conjugated polymers were characterized by NMR, IR, and UV−vis spectroscopies and by CV. These polymers have strong absorption in the visible region, with the absorption peaks shifted to the NIR region upon doping with acids. The ease of the synthesis of the starting polyketone and of the modifications allows large-scale preparation of those conjugated polymers.

Conjugated polymers are of current interest due to their applications in photovoltaics,[1] electrochromics,[2] organic light-emitting devices,[3] and conducting materials.[4] Currently, most applicable conjugated polymers are prepared through step-growth polymerization of specialty monomers.[1b,5] General routes to conjugated polymers via chain growth polymerization remain a challenge.[6] Strictly alternating polyketones are prepared from carbon monoxide and 1-alkenes through catalytic chain-growth polymerization and have not yet found major applications.[7,8] In this Communication we report the preparation of conjugated polymers through postpolymerization reactions of alternating copolymers of styrenic monomers and carbon monoxide (Scheme 1). We have focused our efforts primarily on modification of poly(4-*tert*-butylstyrene-*alt*-CO) (p(^{t}BuS-CO)), since this copolymer can be prepared with high molecular weights and narrow molecular weight distributions and is highly soluble in common organic solvents (as are the modified polymers).[8]

Treating a colorless CH_2Cl_2 solution of p(^{t}BuS-CO) **1** with strong acids such as trifluoromethanesulfonic acid or methanesulfonic acid resulted in a gradual color change over several minutes to a deep blue solution [Supporting Information (SI), Figure S1]. Purging CH_2Cl_2 solutions of p(^{t}BuS-CO) **1** with HBr gas led to similar but slower color changes. Upon addition of a base, the blue CH_2Cl_2 solutions turned orange, and after removal of the solvent, an orange polymer was isolated in high yield. Treating a solution of the orange polymer with acids regenerated the deep blue solution. When HBr gas was used, the deep blue polymer could be isolated as a solid with virtually no residual bromine (<0.3 wt %) based on elemental analysis. (The nature of this initially formed deep blue material will be discussed below.) No color change was observed upon addition of weaker acids such as acetic acid. Typical results of acid-catalyzed modifications of p(^{t}BuS-CO) are shown in Table 1. No significant increase in molecular weight distribution was observed, indicating the absence of chain breaking or cross-linking.

Scheme 1. Postpolymerization Reactions of Alternating Polyketone 1 To Form Conjugated Polymers 2 and 3

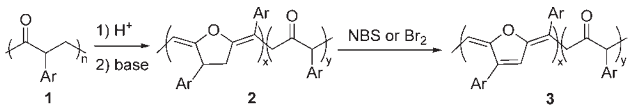

Table 1. Preparation of p(^{t}BuS-CO) 2 via Addition of Various Acids

entry	acid	acid (mg)	degree of modification[a] (%)	M_w[b] (10^3 g·mol^{-1})	M_w/M_n[a]
1-1	$MeSO_3H$	250	86	25.4	1.6
1-2	$MeSO_3H$	30	71	48.5	1.5
1-3	HBr	–	85	31.0	2.0
1-4	CH_3COOH	250	0	–	–

[a] Percentage of repeating units that cyclized. [b] Determined by GPC against polystyrene standards. Reaction conditions: 200 mg of p(^{t}BuS-CO) **1** was dissolved in 10 mL of CH_2Cl_2. After addition of the acid, the reaction mixture was stirred at room temperature for 24 h. P(^{t}BuS-CO) **1** starting material $M_n = 72 \times 10^3$ g·mol^{-1}, $M_w/M_n = 1.25$.

On the basis of IR, NMR, and UV−vis spectroscopic data and elemental analysis, the acid-modified polymer was assigned to structure **2**. The IR spectrum features a large decrease in the carbonyl stretching band at 1760 cm^{-1} and the emergence of a 1561 cm^{-1} band characteristic of a carbon−carbon double bond (SI, Figure S2). Most indicative of structure **2** is the ^{13}C NMR spectrum shown in Figure 1. Signal assignments shown were verified by ^{1}H{^{13}C}-gHSQC and gHMBC experiments. The shifts of vinyl carbons C1, C2, C5, and C6 are consistent with a vinyl ether structure with C2 and C5 α to oxygen appearing at lower fields (156 and 147 ppm) and C1 and C6 β to oxygen appearing at higher fields (109 and 124 ppm). In the gHSQC experiment, C1 is correlated to a low-field-shifted methyne proton at 5.9 ppm. Furthermore, a polymer prepared

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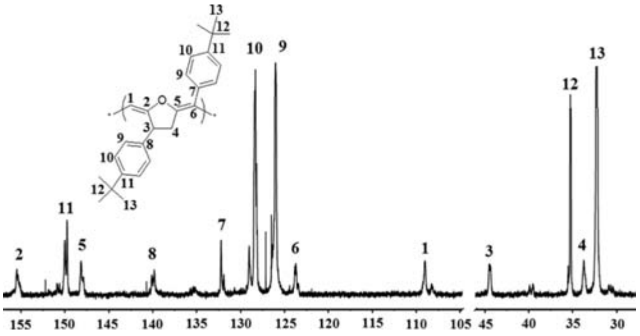
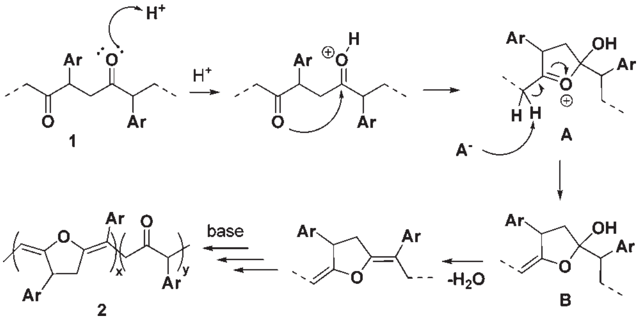
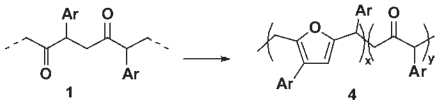


Figure 1. ^{13}C NMR spectrum of p(^{t}BuS-CO) **2** obtained from acid-catalyzed modification of isotactic p(^{t}BuS-CO) **1**.

Scheme 2. Possible Mechanism for the Formation of Polymer 2



Scheme 3. Condensation with Endocyclic Elimination to Yield Polymer 4



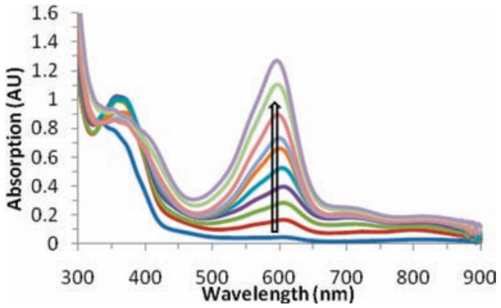


Figure 2. Gradual increase of the 600 nm absorption peak as $MeSO_3H$ was added to a p(^{t}BuS-CO) **2** solution. The 600 nm peak leveled off when the molar ratio of acid to repeating units reached 57:1. Conditions: 1 mg of p(^{t}BuS-CO) **2** was dissolved in 4 mL of CH_2Cl_2 in a standard 10-mm glass cuvette. $MeSO_3H$ (1:100 v/v in CH_2Cl_2) was added dropwise.

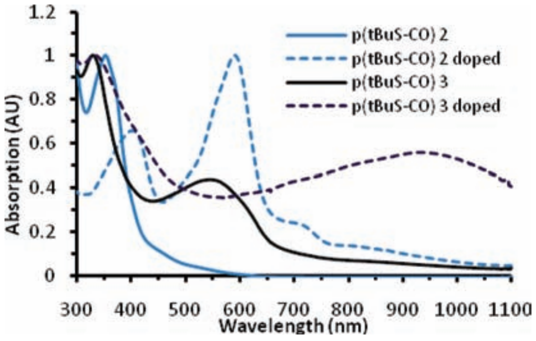


Figure 3. Normalized UV−vis absorption spectra of neutral and acid-doped p(^{t}BuS-CO) **2** and **3**.

from ^{13}CO established that signals assigned to C2 and C5 indeed arise from ^{13}CO. In the labeled polymer, signals assigned to C1 and C6 are doublets showing $^1J_{CC} = 75$ Hz, consistent with structure **2** (SI, Figure S6).

A possible acid-mediated mechanism for the formation of polymer **2** is shown in Scheme 2. Protonation of a carbonyl group followed by intramolecular attack of an unprotonated γ-carbonyl group yields intermediate **A**. Loss of a proton yields the hemiketal **B** which, upon acid-catalyzed dehydration and neutralization, yields polymer **2**.

Since the condensation occurs simultaneously at different positions along the polymer chain, some $-CH_2-C(O)-CH(Ar)-$ units can be trapped between two modified repeating units, and thus full conversion to **2** is not achieved. Statistically, the maximum conversion of monomer units for irreversible condensation reactions on a polymer chain is ca. 86%, assuming all condensations occur at equal rate.[9] Evidence for such trapped ketone units includes a residual ν_{CO} band at 1760 cm^{-1} in the IR spectrum of **2** (SI, Figure S2) and the residual ketone signal in the ^{13}C NMR spectrum (SI, Figure S7). This is especially clear in the ^{13}C NMR spectrum of polymer **2** prepared with labeled ^{13}CO (SI, Figure S6). The degree of conversion of ketone repeating units was determined using the integral ratio of benzylic to vinylic protons (Table 1 and SI). *E*/*Z* isomerism is possible around the C1−C2 and C5−C6 double bonds. We have no evidence concerning which diastereomer is formed or the diastereomeric purity.[10]

Isolated 1,4-diketones are known to undergo acid-catalyzed condensation to yield furans (Paal−Knorr reaction) via mechanism similar to that shown in Scheme 2, with eliminations occurring in an endocyclic rather than an exocyclic manner.[11] Applying this mechanism to **1** yields polymer **4**, which is isomeric with **2** but contains isolated furan units (Scheme 3). NMR spectroscopy cannot unambiguously distinguish **2** from **4**. However, UV−vis spectroscopy offers strong evidence in favor of **2**. Polymer **2** exhibits an intense λ_{max} at 353 nm (Figures 2 and 3). Polymer **4** contains *isolated* furan units, and thus the UV−vis absorption properties should be accurately modeled by simple substituted furans. 2,4-Diphenylfuran exhibits $\lambda_{max} \approx 275$ nm, with no appreciable absorption above 320 nm,[12a] 3-phenylfuran exhibits $\lambda_{max} = 253$ nm,[12b] and 2,5-dimethylfuran exhibits $\lambda_{max} \approx 220$ nm.[12c] Thus, $\lambda_{max} = 353$ nm is inconsistent with isolated furan units and supports structure **2**.[13]

As noted, neutral polymer **2** (Ar = $-C_6H_4C(CH_3)_3$) exhibits a λ_{max} in the UV−vis spectrum at ca. 353 nm. As $MeSO_3H$ was added to a solution of p(^{t}BuS-CO) **2**, a strong band at 600 nm emerged. Neutralization of acid-doped **2** gave the original spectrum back, and this doping/dedoping process is fully reversible over multiple cycles. Figure 2 shows successive additions of $MeSO_3H$ and the increase of the 600 nm band. No difference in NMR and IR spectra between the neutral and acid-doped

Table 2. Electrochemical Data for the Modified Polyketones

entry	polymer	optical bandgap[a] (eV)	electrochemical bandgap (eV)	E_{ox} (V)	E_{red} (V)	HOMO[b] (eV)	LUMO[b] (eV)
2-1	p(^{t}BuS-CO) NBS[c]	1.87	2.08	0.25	−1.83	−4.95	−2.87
2-2	p(^{t}BuS-CO) **3**[d]	1.86	2.04	0.22	−1.82	−4.92	−2.88
2-3	p(S-CO) **3**[d]	1.85	2.03	0.20	−1.83	−4.90	−2.87
2-4	p(ClS-CO) **3**[d]	1.78	2.06	0.39	−1.67	−5.09	−3.03
2-5	P(FS-CO) **3**[d]	1.82	1.96	0.50	−1.46	−5.20	−3.24

[a] Determined by the equation optical bandgap (eV) = 1240/absorption onset. [b] Referenced with the standard ferrocene/ferrocenium redox system. [c] Modified with NBS from p(^{t}BuS-CO) **2**. [d] Modified from **1** with Br_2.

polymers was observed, suggesting that the level of doping is small (SI, Figures S3−S5).

The precise nature of the acid doping of **2** is unclear, but it is thought to be analogous to nonoxidative acid-doping of other conjugated polymers, including poly(phenylenevinylene), polyacetylene, and polythiophene.[14] In these systems it is proposed that protonation yields a carbocation which serves as an internal one-electron oxidant to generate radical cations (polarons) that exhibit absorptions at much longer wavelengths. In the present case, radical cations generated in a similar manner are thought to account for the new absorption peak at ca. 600 nm.

In order to obtain a fully conjugated carbon backbone from polymer **2**, a double bond must be introduced between carbons 3 and 4. This was accomplished by bromination of the benzylic/allylic carbon (carbon 3) followed by elimination of HBr. Initially, *N*-bromosuccinimide (NBS) was used as the bromination agent. Upon heating polymer **2** and NBS at reflux in chloroform, a dark red polymer was isolated. Elemental analysis of this polymer showed no significant residual bromine (<0.5 wt %), which led to the assumption that HBr elimination had already occurred. In the IR spectrum of the dark red polymer, the formation of new C═C double bonds (1656 cm^{-1} and broad 1606−1560 cm^{-1}) was observed (SI, Figure S2). NMR analysis indicated the disappearance of the benzylic and diastereotopic allylic ^1H signals and the disappearance of two high-field shifted carbon signals (carbons 3 and 4). The emergence of a methyne carbon signal was observed at 110 ppm.

The NBS-modified dark red p(^{t}BuS-CO) **3** absorbs strongly in the visible region in its neutral state (λ_{max} = 553 nm). Doping with $MeSO_3H$ resulted in the formation of a light green polymer and appearance of a broad, low-energy band in the NIR region (λ_{max} = 935 nm). A similar green polymer with a less-well-defined NIR band was produced upon treatment of **3** with the strong one-electron oxidant $(p\text{-}BrC_6H_4)_3N^{\bullet+}$. This doping behavior supports the assumption that acid doping occurs in a way similar to oxidative doping, which involves oxidation of the backbone and formation of polarons or bipolarons.[14] The dramatic increase in λ_{max} upon treatment with acid parallels the behavior of polymer **2** and other conjugated polymers.[14c,15] Figure 3 illustrates the UV−vis spectra of neutral and doped p(^{t}BuS-CO) **2** and **3**.

Remarkably, p(^{t}BuS-CO) **3** can be generated directly from polyketone **1** in a one-pot reaction with Br_2 in chloroform. Initially, a dark blue polymer solution formed, indicating the formation of acid (HBr)-doped p(^{t}BuS-CO) **2**. Upon raising the temperature of the solution, bromination of **2** followed by elimination of HBr yielded **3**. Removal of solvent, HBr, and excess Br_2 gave dark red **3** containing a very low quantity of residual bromine (<1.0 wt %).

The one-pot bromine modification procedure was applied to other less soluble styrenic polyketones, including poly(styrene-*alt*-CO) (p(S-CO)), poly(4-chlorostyrene-*alt*-CO) (p(ClS-CO)), and poly(4-fluorostyrene-*alt*-CO) (p(FS-CO)). The resulting polymers **3** are soluble in CH_2Cl_2 and THF; p(FS-CO) **3** is also soluble in acetone. As a result of the *tert*-butyl substituent, p(^{t}BuS-CO) **3** is soluble in a much wider range of solvents, including hydrocarbon solvents such as hexane.

The electrochemical band gaps of various derivatives of **3** determined by CV agree with their optical absorptions (Table 2). When electron-withdrawing groups (-Cl, -F) are attached to the phenyl ring, the band gaps remain the same but the HOMO/LUMO levels are lowered, which agrees with literature precedent.[16] However, despite strong optical absorption of the polymers, no significant emission was detected.

In summary, a new class of conjugated polymers was synthesized by postpolymerization reaction of poly(4-*tert*-butylstyrene-*alt*-CO), **1**, a chain-growth polymer prepared from Pd(II)-catalyzed copolymerization of 4-*tert*-butylstyrene and carbon monoxide. Upon treatment of **1** with strong acids, an intramolecular condensation reaction occurs to form **2** with a poly(2,5-dimethylenetetrahydrofuran)-type backbone interspersed with some “trapped” monomer units. A polymer fully conjugated through the carbon backbone, **3**, was obtained by bromination of **2** followed by loss of HBr. Upon doping with strong Brønsted acids, the neutral polymers **2** and **3** exhibit dramatic shifts of λ_{max} to higher wavelengths. In the case of **3**, the low-energy band appears in the NIR region. This chemistry has been extended to polyketones prepared with other styrenic monomers. These conjugated polymers are attractive in that they are easily prepared from readily available monomers, molecular weights can be controlled, they are thermally stable, and certain derivatives have high solubility in nonpolar solvents. Potential applications of these new polymers are under investigation.

■ ASSOCIATED CONTENT

S Supporting Information. Preparation of polymers **2** and **3** and detailed experimental results (NMR, IR, UV−vis spectra, TGA, and DSC graphs). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Note in Figure 1, in addition to the ^{13}C signal at 109 ppm assigned to C1, there is a minor resonance at 108 ppm which may correspond to a minor diastereomer.

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(13) Scheme 2 is one of several possible pathways leading to **2**. Furan units and/or endocyclic double bonds could be formed, but under acid conditions rearrangement to more stable exocyclic, conjugated structures could occur.

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