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Synthesis and Characterization of Soluble, Ionically Functionalized Polyacetylenes

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Introduction. Substituted conjugated polymers have been extensively studied in efforts to elucidate fundamental structure/property relations and to identify soluble or fusible derivatives to aid in commercial processing. Although poor ambient stability diminishes their technological importance, polyacetylene and its derivatives serve as central model compounds in the study of conjugated polymers. Here we report the synthesis of *p*olyacetylene *c*ationic and *a*nionic ionomers ($\mathbf{P_C}$ and $\mathbf{P_A}$) from the ring-opening metathesis polymerization (ROMP) of alkylammonium and sulfonate functionalized cyclooctatetraenes, respectively, using the well-defined tungsten alkylidene catalyst **1** [W=CH(*o*-C_6H_4OMe)(NC_6H_5)[$OCCH_3(CF_3)_2$]$_2$(THF); THF = tetrahydrofuran] (Scheme 1).[1] The thermodynamically stable trans forms of these polymers are soluble in certain polar solvents, are extensively π-conjugated, and are electrically conductive when oxidatively doped with iodine. Such properties are unusual for soluble polyacetylene derivatives that typically exhibit so little π-conjugation that they are white or yellow in color[2−4] and exhibit relatively low iodine doped conductivities ($<10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$).[5,6] Although **1** reacts rapidly with a wide variety of polar or protic substituents, the weakly basic sulfonate and relatively inert alkylammonium moieties studied herein did not prevent polymerization. Previous reports on the ROMP of substituted cyclooctatetraenes (R−COTs) using alkylidene catalysts such as **1** have been primarily limited to nonpolar alkyl or aryl substituents with very few of the resulting poly(R−COT)s observed soluble in the trans form.[7−10]

The polymers reported herein represent an uncommon example of structurally similar anionic and cationic conjugated ionomers that can potentially be both reductively and oxidatively doped. As such, they represent excellent model compounds to study conjugated ionomers at both the fundamental level and in new device technologies.

Results and Discussion. Monofunctionalized cyclooctatetraene (R−COT, R= $-CH_2CH_2SO_3TMA$ or $-CH_2CH_2NMe_3OTf$, OTf = $CF_3SO_3^-$, TMA = Me_4N^+) was treated with **1**,[1] as shown in Scheme 1, to produce a poly(R−COT) with ionic functionalities by ring opening metathesis polymerization. Both $\mathbf{P_C}$ and $\mathbf{P_A}$ are dark blue solids that are soluble in dimethyl sulfoxide (DMSO) (> 1 mg/mL) as evidenced by clean filtration through a 0.2 μm filter (see Figure 1).[11,12] Additionally, $\mathbf{P_C}$ is also soluble in *N,N*-dimethylformamide, another highly polarizable solvent. Perhaps most useful, $\mathbf{P_A}$ is also soluble in methanol (>1 mg/mL) and ion exchanging to the sodium salt imparts water solubility to this anionically functionalized polyacetylene analogue.

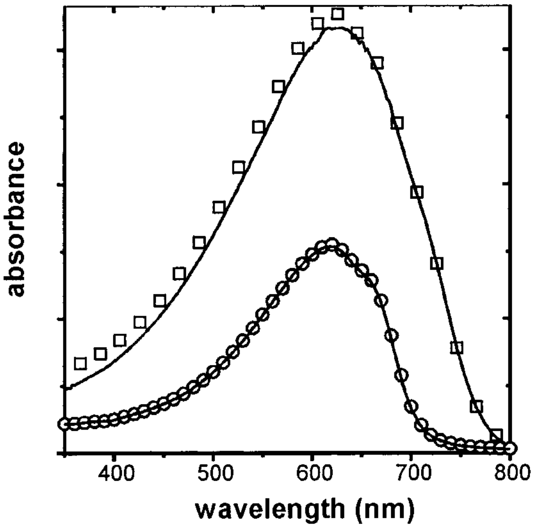
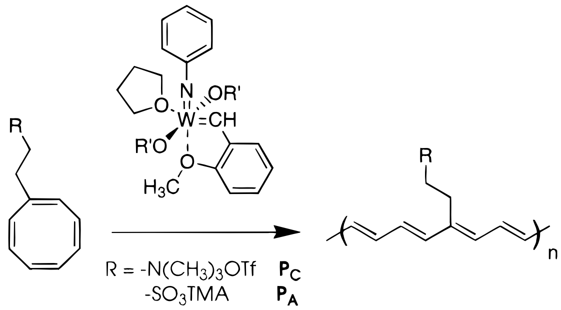


Figure 1. Absorbance spectra of solutions of $\mathbf{P_C}$ (○) and $\mathbf{P_A}$ (□) in DMSO before and after (lines) filtration through a 0.2 μm filter.

Scheme 1. Ring Opening Metathesis Polymerization of Substituted Cyclooctatetraenes (OTf = $CF_3SO_3^-$, TMA = $(CH_3)_4N^+$, R′ = $-CCH_3(CF_3)_2$)



Characterization by proton nuclear magnetic resonance spectroscopy (^{1}H NMR), absorbance spectroscopy and gel permeation chromatography (GPC) provides evidence for polymeric structures. The ^{1}H NMR spectra of both polymers in d_6-DMSO are broadened relative to the corresponding monomer spectra, as expected due to slowed molecular tumbling. With the exception of the backbone/ring protons, chemical shifts are similar between the monomers and corresponding polymers. In both $\mathbf{P_A}$ and $\mathbf{P_C}$, broad resonances between 6.0 and 7.2 ppm are assigned to the backbone protons. The downfield shift of the polymer backbone ^{1}H resonances relative to those for the monomer ring protons ($\delta = 5.8$ ppm) indicates a higher degree of conjugation in the ROMP products.

The UV/vis absorbance spectra of these polymers are shown in Figure 1 with the wavelengths of maximum absorbance ($\lambda_{\max}$) summarized in Table 1. Both $\mathbf{P_C}$ and $\mathbf{P_A}$ show a single $\lambda_{\max}$ in DMSO near 620 nm (2.0 eV) with similar values observed for thin solid films. These values are highly red shifted from the absorbance maxima of the nonplanar monomers ($\lambda_{\max} = 288$ nm, DMSO) due to substantially increased π-conjugation. On the basis of extrapolation of data for well-defined polyene oligomers, the energies obtained for both $\mathbf{P_A}$ and $\mathbf{P_C}$ correspond to conjugation lengths of 20−40 double bonds.[13] The absorbance maxima of the polymers in

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Table 1. Physical Properties of *trans*-Poly(R−COT)

R	λ_{max}/nm^a monomer	λ_{max}/nm^a polymer	M_w^{b}	M_n^{b}	PDI	σ (Ω^{-1} cm^{-1})^c
$-CH_2CH_2NMe_3OTf$	288	614	*d*	*d*	*d*	1−0.01
$-CH_2CH_2SO_3TMA$	288	624	103 000	35 000	2.9	0.7−0.4

[a] In DMSO. [b] Compared to TMAPSS standards in 0.4% (w/v) (TMA)BF$_4$ in DMSO.[17] [c] Iodine-doped films measured by four-point probe. [d] Not measured.

solution did not shift to lower energy with time as has been observed for nonionic poly(R−COT)s that undergo thermodynamically favorable cis−trans isomerizations.[9,14] Therefore, the observed $\pi-\pi^*$ transitions are assigned to the predominately trans conformations.

Comparison of the GPC elution time profile for **P$_A$** to the elution times observed for narrow TMAPSS (PSS = poly(styrene sulfonate)) standards yielded an apparent molecular weight, M_n, of 35 000 (≈970 double bonds) and a polydispersity index (PDI) of 2.9. These GPC data are simply taken to indicate that **P$_A$** is polymeric. As has been discussed by numerous authors, the quantitative accuracy of GPC depends on how well the standards mirror the solution conformational structure of the polymer under study.[15,16] Furthermore, with ionomers, specific polymer−column interactions often result in separation on the basis of other than simple size-exclusion. The addition of salt to the eluent (as in the present studies) and the use of polyelectrolyte standards may minimize such effects, but the hydrodynamic radius of the rigid trans polymers is still likely expanded relative to the more flexible PSS standards employed.[17] Strong adsorption of **P$_C$** to the GPC columns prevented its characterization by this technique.

The extended π-conjugation of **P$_A$** and **P$_C$** raises the possibility for interesting electronic properties. Both are insulators in the undoped state and electronically conductive when doped with iodine vapor. The conductivity data are summarized in Table 1. Values from 1 to 0.01 Ω^{-1} cm^{-1} and 0.7−0.4 Ω^{-1} cm^{-1} were obtained for **P$_C$** and **P$_A$**, respectively, with the precise value apparently depending on the age of the polymer, the degree of doping, the film thickness, and the length of time between doping and the measurement.

The combination of solubility in the undoped state with extensive π-conjugation and relatively high iodine-doped conductivity, as observed for **P$_C$** and **P$_A$**, is unusual for both polyacetylene derivatives and poly(R−COT)s. Soluble polyacetylene derivatives from the polymerization of mono- and disubstituted acetylenes are typically white or yellow in color (λ_{max} = 270−300 nm)[2,4,5] and exhibit iodine doped conductivities less than 10^{-3} Ω^{-1} cm^{-1}.[3,5,6] These short conjugation lengths, as reflected by relatively low λ_{max} values, result from steric interactions involving the substituents that force the polymer backbone out of planarity. Perhaps surprisingly, a class of soluble, ionically functionalized polyacetylenes from the polymerization of 2-ethnylpyridium salts has reportedly exhibited high degrees of π-conjugation despite a high degree of substitution.[18] The corresponding iodine-doped conductivies of these and other polyacetlyene ionomers, however, are less than 10^{-3} Ω^{-1} cm^{-1}.[18,19]

Extensive π-conjugation has been observed for a number of poly(R−COT)s owing to a relatively low substituent density. The reduced density of side chains, however, renders the majority of these polymers insoluble in the trans form. In the work of Gorman et al., only poly(R−COT)s with secondary or tertiary substitution α to the backbone were observed to be soluble in the trans form. The additional chain branching, however, resulted in a decrease in conjugation length relative to that observed for primary substitution. Of the soluble *trans*-poly(R−COT)s reported, none were observed to exhibit absorbance maxima greater than 586 nm or iodine-doped conductivities greater than 0.2 Ω^{-1} cm^{-1}. The tradeoff between solubility and conjugation length was further illustrated by studies on copolymers that led to the proposal that poly(R−COT)s with λ_{max} greater than 580−90 nm would be insoluble.[9,11c,20]

As observed with other conjugated polymers, the introduction of ionic moieties can provide the driving force necessary to solubilize rigid, highly conjugated polymers.[21,22] The possibility for specific ion−dipole interactions between polymer and solvent as well as potential entropic gains from counterion dissociation help drive dissolution without the need for increased side-chain branching or decreased persistence length. Herein, such an approach has been successfully used to prepare soluble *trans*-poly(R−COT) derivatives with much higher degrees of conjugation than previously thought possible.

In summary, ROMP of ionically functionalized cyclooctatetraenes provides a versatile route for the production of conjugated ionomers. The ionomers reported are uncommon examples of soluble, highly conjugated *trans*-poly(R−COT)s. Iodine doping produces electrical conductivities orders of magnitude larger than observed for other soluble polyacetylene derivatives and the highest yet reported for soluble *trans*-poly(R−COT)s. The observed combination of solubility with relatively high iodine-doped conductivity and extensive π-conjugation is largely due to the ability of ionic functionality to impart solubility without requiring a high degree of substitution or side-chain branching.

Experimental Section. All polymerization reactions are air and moisture sensitive and were performed in a nitrogen-filled drybox. Both monomers were thoroughly dried under vacuum (60 °C, 20 mTorr) for greater than 24 h. NMR spectra were recorded with a Varian INOVA 300 MHz spectrometer. Ultraviolet−visible absorption spectroscopy was performed on a Hewlett-Packard 8452A diode array spectrometer. Gel permeation chromatography was performed on a Waters chromatography system utilizing an HR4 size exclusion column, a 510 pump, and a 996 photodiode array detector with 0.4%(w/v) (TMA)BF$_4$ in DMSO as eluent. TMAPSS standards were prepared by ion exchange from narrow NaPSS standards (American Polymer Standards). Conductivity was measured by the four-point probe method with a Solartron Instruments 1287 electrochemical interface. Film thickness was measured with a Starrett electronic micrometer, no. 733.

The tungsten catalyst $[W{=}CH(o\text{-}C_6H_4OMe)(NC_6H_5)[OCCH_3(CF_3)_2]_2(THF)]$ was prepared as described in the literature.[1] Tetramethylammonium tetrafluoroborate (Aldrich) and *N*,*N*-dimethylformamide (Fisher) were used as received. Toluene (Fisher) was distilled from sodium benzophenone. Methylene chloride (Fisher) was distilled from calcium hydride. Both toluene and methylene chloride were freeze−pump−thaw degassed prior to use.

In a typical polymerization, as described for poly($C_8H_7CH_2CH_2NMe_3OTf$), 25 mg (0.002 mmol) of catalyst was added to a solution of 150 mg (0.04 mmol) of C_8H_7-$CH_2CH_2NMe_3OTf$ in 200 μL of CH_2Cl_2. The solution was shaken briefly to ensure mixing and then allowed to set for 12 h. The solvent was removed by vacuum, and the remaining dark solid was rinsed with toluene until the rinses were colorless. Typical yields were 60−70%. Films for conductivity studies were prepared by the dropwise application of a DMSO polymer solution to a glass slide. The solvent was removed, and the film was dried under vacuum (20 mTorr) for greater than 12 h prior to doping. Oxidatively doped films were prepared by exposure to iodine vapor for 1 h followed by removal of volatile iodine under vacuum (20 mTorr) for 1 h.

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Supporting Information Available: Text giving details of the monomer syntheses and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Poly(R−COT), where R = H, is structurally equivalent to polyacetylene, $(CH)_n$. The nomenclature emphasizes the synthetic differences between the two and allows for the potential for unintended structural differences arising from the different syntheses.

(11) This does not exclude the possibility of aggregation that has been observed for some solubilized polyacetylene copolymers. See for example: (a) Cuniberti, C.; Piaggio, P.; Dellepiane, G.; Catellani, M.; Piseri, L.; Porzio, W.; Tubino, R. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 471−476. (b) VanNice, F. L.; Bates, F. S.; Baker, G. L.; Carrol, P. J.; Patterson, G. D. *Macromolecules* **1984**, *17*, 2626−2629. (c) Krouse, S. A.; Schrock, R. R. *Macromolecules* **1988**, *21*, 1885−1888.

(12) $\mathbf{P_C}$ was also found to be soluble (>1 mg/mL) in dimethylpropyleneurea (DMPU), another polarizable, polar solvent. The high boiling point (146 °C/44 mmHg) of DMPU precludes its usefulness for our work.

(13) Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 7989−8004. Comparison of the maximum absorbance of $\mathbf{P_C}$ and $\mathbf{P_A}$ in DMSO to the extrapolation of the values obtained by Knoll and Schrock in pentane gives a value of 40 double bonds for the conjugation length, while comparison to the values obtained in carbon disulfide gives 20 double bonds for the conjugation length.

(14) In previous studies of the ROMP of R−COTs, the polymerization is generally observed to proceed with the initial formation of the cis isomer with subsequent isomerization to the thermodynamically more stable trans form.[9] During preliminary investigations utilizing relatively low monomer-to-catalyst ratios and short reaction times, an additional absorption with λ_{max} at 382 nm was observed for $\mathbf{P_A}$. The position of this shorter wavelength absorption is similar to that observed for the predominantly cis isomer of other poly(R−COT)s. Upon irradiation with an unfiltered tungsten light source for 1−3 h, this shorter wavelength 382 nm absorption disappears leaving only the longer wavelength absorption assigned to the predominantly trans isomer. Presumably, the relatively long reaction times in the present study prevented observation of the cis form.

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(17) PSS standards were chosen to mimic ionic effects of $\mathbf{P_A}$. The charge repulsion effect was overcome by the addition of 0.4% (w/v) $(TMA)BF_4$. With the exception of the absence of salt resulting in polymer exclusion, the several salt concentrations investigated had minimal effect on the resulting molecular weight when compared to standards at the same salt concentration.

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(20) It is noted that comparison of λ_{max} values is only considered semi-quanitative because of differences in solvent and the distribution of chain lengths.

(21) Ionic functionalities have been utilized to impart water solubility to several conjugated polymers. See for example: (a) Patil, A. O.; Ikenoue, F.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1858−1859. (b) Yue, J.; Epstein, A. J. *J. Am. Chem. Soc.* **1990**, *112*, 2800−2801. (c) Child, A. D.; Reynolds, J. R. *Macromolecules* **1994**, *27*, 1975−1977, (d) Sundaresan, N. S.; Basak, S.; Pomerantz, M.; Reynolds, J. R. *J. Chem. Soc., Chem. Commun.* **1987**, 621.

(22) Further supporting the ability of the ionic functionalities to impart solubility, a nonionic analogue to $\mathbf{P_C}$, poly{[$(CH_3)_3CCH_2CH_2$]COT)}, prepared in our laboratory is insoluble in DMF and DMSO.

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