Copolymerization **Hot Paper**

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TEMPO Containing Radical Polymonothiocarbonate Polymers with Regio- and Stereo-Regularities: Synthesis, Characterization, and Electrical Conductivity Studies

Gulzar A. Bhat, Ahmed Z. Rashad, Xiaozhou Ji, Manuel Quiroz, Lei Fang, and Donald J. Darensbourg**

Abstract: *We report the synthesis of a (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl) (TEMPO) appended polymonothiocarbonates through the ring-opening copolymerization of (4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl) (GTEMPO) in the presence of carbonyl sulfide under ambient conditions. We have prepared the atactic and isotactic versions of this polymer, using enantiopure R or S forms of the GTEMPO monomer in the latter instances. Cyclic voltammetry studies revealed both oxidation and reduction events that were characteristic of TEMPO radicals. Electrical conductivity of these polymers was measured as solid-state films after annealing the samples above their glass transition temperatures. At room temperature the isotactic polymer shows much greater conductivity (ca. 10^{-4} S cm^{-1}) than the atactic (ca. 10^{-7} S cm^{-1}), attributed to the well-defined stereochemistry and regulated charge transport pathway of isotactic polymer chains in contrast to the irregular structure of the atactic counterpart.*

Recently, interest in redox active radical polymers have garnered significant attention as functional materials in the fields ranging from organic electronics,[1–5] energy storage,[6–9] high performance conductors,[10,11] high-efficiency solar cells,[12,13] light-emitting devices,[14,15] electrochromism,[16] organocatalysis,[17] biological imaging agents[18–20] and other energy related modules. This is primarily due to these polymers intrinsic potential to offer chemical and electrochemical tunable solutions for applications which are traditionally dominated by metals. Among the diverse macromolecular redox active polymers, 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) containing polymers are well studied because of their high innate stability, fast and reversible redox kinetics, and ease of functionalization.[21] The first radical polymer, (2,2,6,6-tetramethyl piperidinyl oxymethacrylate) (PTMA) was synthesized by functionalizing polymethacrylate (PMA) with stable radical TEMPO moieties by Griffith and co-workers in 1967.[22] Later, Kishita and co-workers reported that the nitroxide groups in these redox active polymers were reversibily oxidized to oxiammonium cations, which following two decades of research have resulted in their use as the positive electrode (cathode) in rechargeable batteries.[23–26]

The early electrical conducting materials explored were polymers with π-conjugation along their molecular backbones, which were later doped to achieve higher conductivities.[27,28] Subsequently, it was evident that most of these polymers have several drawbacks, such as a lack of optical transparency in the visible region, complicated synthesis, poor processability and low stability as the result of different dopants. These issues were addressed by Boudouris and co-workers who examined the solid state electrical conductivities of charge neutral radical polymers having open shell stable pendant radical moieties.[29] The initial studies of these type of radical polymers culminated in 2018 of polymers with an electrical conductivity of 28 S m^{-1}.[30] The pathway for charge transport in these organic radical polymers is thought to be electron or hydrogen hopping from radical site to radical site with concomitant sequential motion of the polymer chains.[31] It was further deduced from these studies that the backbone structure of these radical polymers can significantly affect their conductivity. Figure 1 lists a comparable group of TEMPO based polymers with various polymer backbones. Despite these significant advances made in this field, it is still a great challenge to develop feasible synthetic methodologies for these radical-pendant polymers with full control of the regiochemistry.

Inspired by the recent report by Savoie, Boudouris and co-workers on the polyether produced by the ROP of an epoxide containing a TEMPO substituent (GTEMPO),[30] we have employed this epoxide to synthesize monothiocarbonate polymers featuring pendant radical TEMPO moieties. This was accomplished using the ring-opening copolymerization (ROCOP) methodology employing the well-defined binary

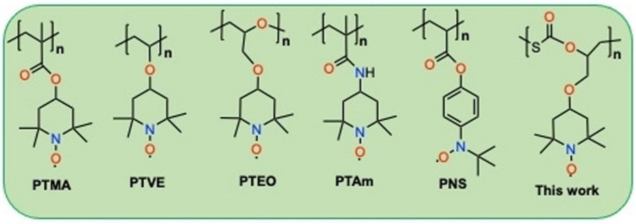

Figure 1. Comparison of radical polymers having different backbones.

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catalytic system of (salen)CrCl/PPNCl. A major advantage of this procedure is that it provides an uncomplicated synthetic route to both regio- and stereo-regular radical polymers. That is, using rac- or (*R* or *S*)-epichlorohydrin it is possible to prepare large quantities of a TEMPO containing epoxide monomer in a single step. This coupled with the fact that the ring-opening of the TEMPO epoxide during the copolymerization with carbonyl sulfide (COS) occurs highly regioselectively at the less-hindered methylene carbon, affords stereoregularity in the copolymer consistent with that of the epoxide monomer. In this manner, we have prepared a regioregular atactic copolymer from *rac*-GTEMPO and COS, as well as the isotactic versions using the enantiopure R and S forms of the GTEMPO monomer. Furthermore, this process can be easily scalable to the kilogram level. Herein, we have examined the solid-state electrical conductivities of these radical copolymers, and have shown that the polymers with controlled stereochemistries (*R* or *S*) display much better conductivity than their stereoirregular analogues.

The epoxide monomer, GTEMPO was synthesized as previously described from epichlorohydrin and 4-hydroxy-2,2,6,6-tetramethylpiperidin-*N*-oxy.[32] Attempts at copolymerizing GTEMPO with CO_2 were not successful in the presence of well-defined (salen)CoCl and (salen)CrCl binary catalyst systems at ambient temperature. Instead, when the coupling reaction of GTEMPO and CO_2 was carried out at 80 °C using the (salen)CrCl/PPNCl catalyst, a cyclic organic carbonate product was obtained. The compound was fully characterized spectroscopically (SI) and crystallographically (Figure 2). As we have previously noted, epoxides which are unreactive with CO_2 under these conditions are often reactive with carbonyl sulfide. Indeed, this was shown to be the case as described below.

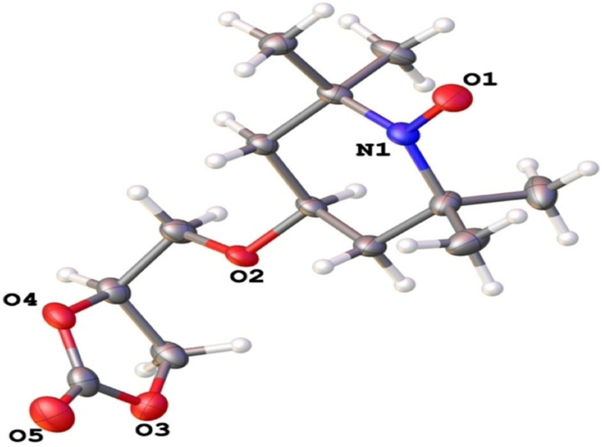
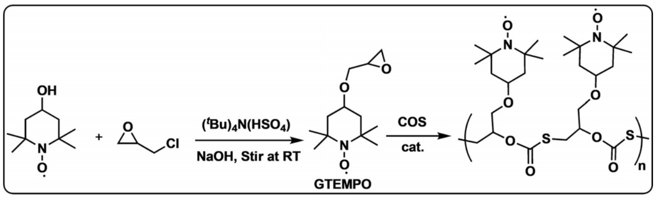


Figure 2. X-ray crystal structure of the cyclic carbonate derived from GTEMPO and CO_2. N–O distance of 1.285 Å.[35]



Scheme 1. Synthesis of radical containing copolymers using COS and GTEMPO.

Copolymerization of *rac*-GTEMPO and COS was performed in a 1:1 solvent of dichloromethane/toluene in a stainless steel reactor at ambient temperature in the presence of (salen)CrCl/PPNCl catalyst at a pressure of 1.0 MPa (Scheme 1). This ROCOP reaction pathway represents the first reported preparation of a polymer containing pendant TEMPO groups utilizing this strategy. Although the coupling of COS and GTEMPO is highly selective at room temperature for copolymer formation, at 70 °C both cyclic and polymeric monothiocarbonate are produced. Table 1 contains the copolymers obtained at different monomer loading, where the molecular weights were controlled by the amount of trace water or hydrolyzed epoxide (CTA) in the epoxide monomer.

Table 1: Summary of the copolymerization of GTEMPO and COS using different equivalents of the GTEMPO monomer.[a]

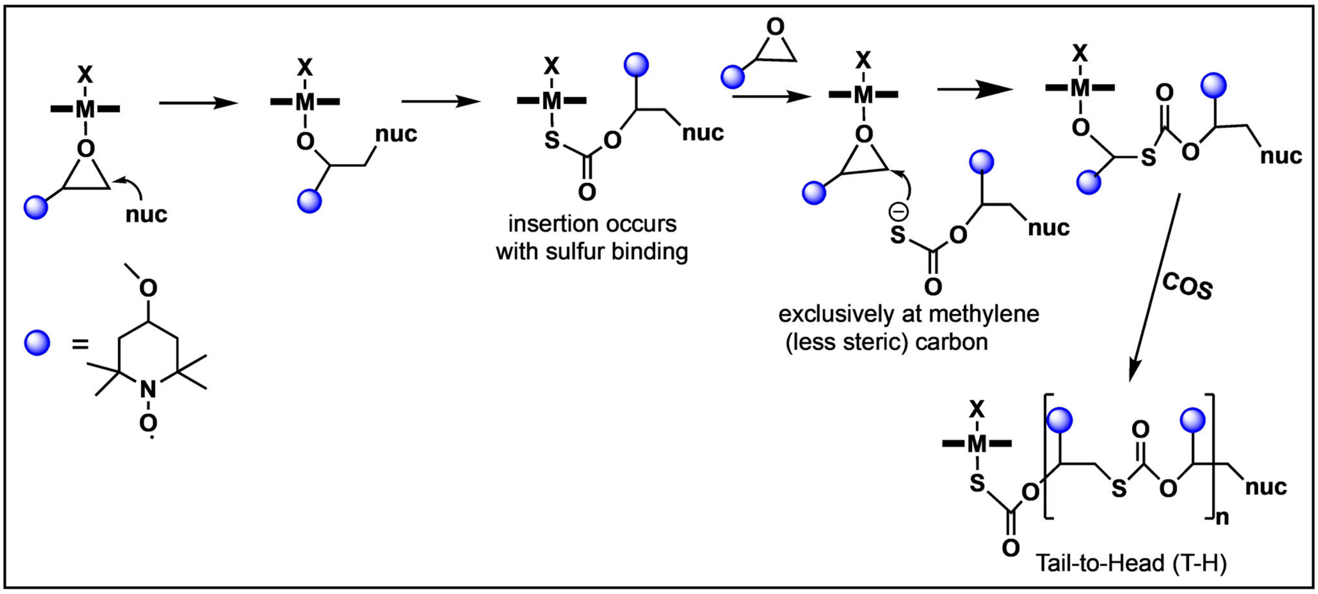
Entry	Monomer/Cat/Co-Cat	M_n [kg mol^{-1}]	PDI
1	250:1:1	10.8	1.6
2	500:1:1	11.1	1.77
3	750:1:1	11.3	1.76

[a] Reaction conditions: ambient temperature in DCM/toluene at 1.0 MPa for 24 h. The polymers are atactic. Molecular weight is controlled by water in monomer.

In our and others previously reported studies, the copolymerization reaction of mono-substituted epoxides with bulky electron-donating substituents, ring-opening occurs highly selectively at the methylene carbon with COS insertion with metal sulfur bonding, resulting in formation of tail-to-head copolymers as depicted in Scheme 2.[33] Hence, upon utilizing enantiopure R or S versions of the GTEMPO monomer (synthesized from R- or S-epichlorohydrin) should afford isotactic polymonothiocarbonate copolymers (see below).

Formation of these radical copolymers was confirmed by (IR, ^{1}H and ^{13}C NMR, EPR, MALDI-ToF) spectroscopies. That is, the FTIR spectrum shows the characteristic monothiocarbonate peak at 1718 cm^{-1} in addition to the peaks due to the GTEMPO monomer, and the ^{1}H NMR spectrum of the radical quenched sample clearly supports ROCOP of the GTEMPO monomer (see SI for details). In the radically quenched ^{13}C NMR spectrum of the T-H atactic copolymer two ^{13}C signals are evident, whereas, as anticipated only one ^{13}C signal is observed for the isotactic polymers (Figure 3 a). ^{1}H NMR showed no quantifiable ether linkages in the copolymer, and there were no O/S exchange processes noted in the ambient temperature copolymerization process as indicated by FTIR and ^{13}C NMR spectroscopies.

Further characterization of the copolymers provided by the polymerization of COS and GTEMPO was obtained by MALDI-ToF spectroscopy. In Figure 3 b is shown the MALDI spectrum of the low molecular weight portion of the copolymer prepared (entry 1 of Table 1), which depicts



Scheme 2. Mechanistic pathway for the formation of tail-to-head copolymer.

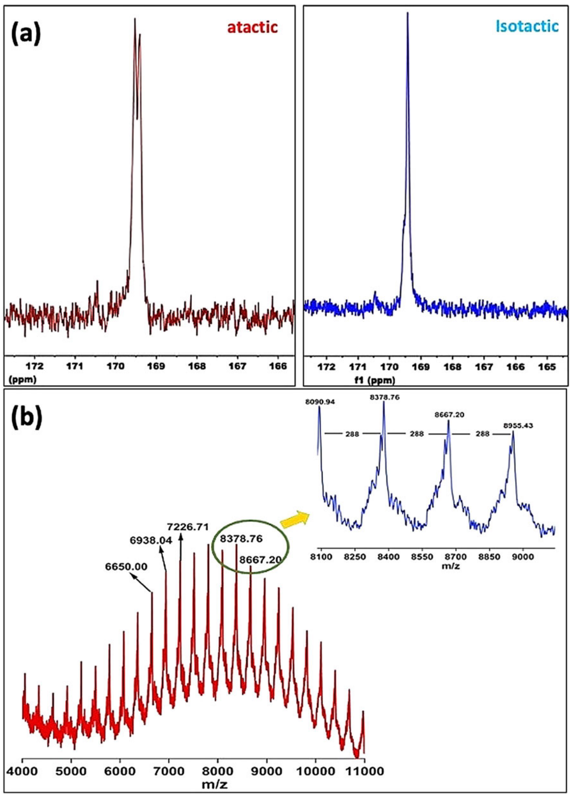


Figure 3. a) Comparison of carbonyl ^{13}C NMR region of the isotactic and atactic radical copolymers. b) MALDI-ToF spectrum of radical copolymer produced in entry 1 of Table 1.

a single series of peaks with a separation of 288 *m*/*z* which corresponds to the mass of the repeat unit GTEMPO/COS. More detailed analysis reveal the hydrolyzed GTEMPO monomer serves as the chain-transfer agent.

The paramagnetic nature of these radical copolymers was established by electron paramagnetic resonance (EPR) spectroscopic studies in solution. The EPR spectra of these copolymers exhibit a single signal centered around 3280 G rather than showing hyperfine splitting owing to nitrogen atoms ($I=1$) (Figure S15). This has also been seen in the literature for high molecular weight radical polymers, where the exchange interaction between closely spaced radicals quenches the hyperfine-induced triplet line shape of the TEMPO molecule in solution.[34] The g-value in these TEMPO based polymers is quite similar to that of the free electron ($g=2.0023$).

The thermal stability of both atactic and isotactic copolymers were determined by thermal gravimetric analysis (TGA). These measurements revealed that these copolymers are thermally stable, with the temperature at which 50 % of the polymer remains (T_{d50}value) is around 270 °C as indicated in Figure 4. DSC curves of all the copolymers showed T_gs of around 58 °C.

To gain insight into the redox behavior of these radical copolymers, cyclic voltammograms of polymer samples were recorded in DMF solutions. Measurements were carried out at ambient temperature under argon using 0.1 M [^{t}Bu$_4$N][PF$_6$] as the supporting electrolyte, and referenced to Fc$^{+/0}$ ($E_{1/2}=$ 0.0 V) as an internal standard. Commencing in the anodic direction, both atactic and isotactic copolymers have a reversible oxidation at almost identical potentials ranging from 0.25 to 0.28 V, which are assigned to the oxidation of the TEMPO moieties (Figure 5).

These values are similar to that of the pure monomer (GTEMPO). Upon scanning in the opposite direction these radical copolymers exhibit a reversible reduction that is associated with a one electron event on the TEMPO moieties with essentially identical potentials ranging from −1.95 to −1.98 V. As observed in the pure monomer, the irreversibility of this reduction event was confirmed upon increasing the scan rates. Full scans and scan rate dependence of GTEMPO, isotactic (*R* and *S*), and atactic copolymers are indicated in

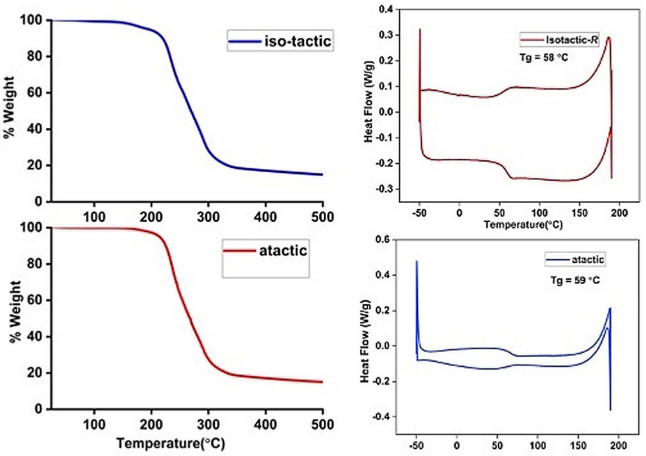


Figure 4. TGA and DSC curves of the atactic and isotactic radical copolymers.

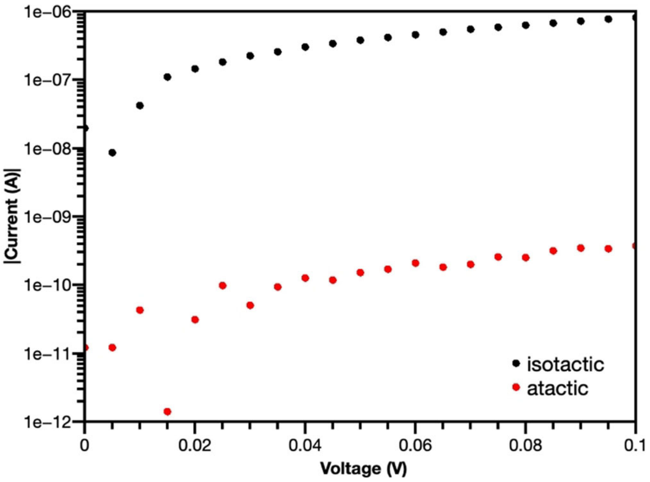


Figure 6. Comparison of solid-state electrical conductivity of isotactic and atactic radical copolymers measured as solid-state films on gold electrodes.

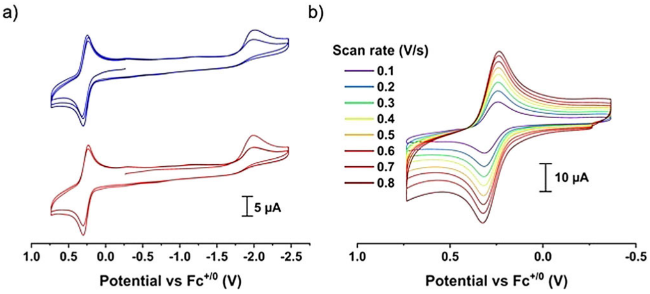


Figure 5. a) Cyclic voltammogram plot of atactic polymer. b) Scan rate dependence for the reversible redox couple of atactic polymer.

Figures S17–S19, respectively. Scan rate dependent CVs confirmed diffusion-controlled electrochemical processes by exhibiting a linear correlation between the cathodic peak currents at the TEMPO reduction and the square root of the scan rate.

Of most importance to our motivation for synthesizing these radical polymonothiocarbonate polymers is an examination of their electrical conductivity properties. In particular, to evaluate any difference in electron mobility in proceeding from atactic to isotactic polymer structures. Among the numerous factors influencing electron transport along the polymer chains in these radical polymers should be the distance between radical centers. This specific separation would be expected to be much greater for atactic vs. isotactic polymers. Other considerations are the film morphology, free volume between chains, and percolation pathways, which are all expected to differ for atactic and isotactic polymers. Herein, we measured the electrical conductivities of these radical polymers as solid-state films deposited on gold electrodes. The solid-state devices were annealed above the T_g values of the polymers before performing measurements. Both atactic and isotactic polymers are fully amorphous as revealed by PXRD. At ambient temperature, the isotactic polymers exhibited greater conductivity (ca. 10^{-4} S cm^{-1}) than the atactic analog ($\approx 10^{-7}$ S cm^{-1}; Figure 6). This can be attributed to the higher packing order originating from the isotactic polymer chains. In the temperature-dependent measurements, the polymer samples were heated in a vacuum probe station and held at the desired temperature for 10 min before collecting conductance data. For both isotactic and atactic polymers, conductivity increased above their T_g values as a result of thermal activated transport. However, no obvious correlation between temperature and conductivity was noted within the high temperature region (Figure S21) as the electrical behavior can be interfered with by multiple factors, such as defects and impurities.

Herein, we have synthesized regio-regular TEMPO containing radical polymers by the (salen)CrCl/PPNCl catalyzed copolymerization of a TEMPO substituted epoxide and carbonyl sulfide. In a similar manner, isotactic copolymers were prepared from the enantiopure (R and S) versions of the epoxide. These copolymers were fully characterized by spectroscopic (IR, ^{1}H and ^{13}C NMR, EPR, MALDI) and thermal (TGA, DSC) techniques. Electrical conductivity measurments of films of these copolymers deposited on gold electrodes were determined at ambient temperature, clearly indicating that the isotactic polymers displayed an electrical conductivity value of about 10^{-4} S cm^{-1} which is much greater than that of its atactic analogue (ca. 10^{-7} S cm^{-1}). To put this in perspective, PTMA is reported to have an electrical conductivity of about 1×10^{-6} S cm^{-1}.[29]

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: carbonyl sulfide · copolymerization · electrical conductivity · epoxides · TEMPO

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[35] Deposition Number 2090114 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Communications

Copolymerization

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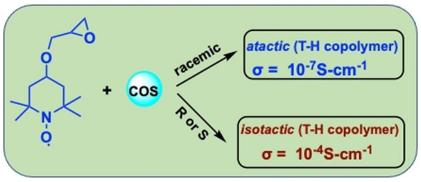
TEMPO Containing Radical Polymonothiocarbonate Polymers with Regio- and Stereo-Regularities: Synthesis, Characterization, and Electrical Conductivity Studies



The preparation of atactic and isotactic radical polymonothiocarbonates by the copolymerization of a TEMPO derived epoxide and carbonyl sulfide (COS) in the presence of the metal catalyst (salen)CrCl/PPNCl is reported. It was uncovered that there is a significant enhancement of the electrical conductivity of the isotactic copolymer (ca. 10^{-4} S cm^{-1}) as compared to that of the atactic copolymer (10^{-7} S cm^{-1}).