CONDUCTING POLYMERS

A nonconjugated radical polymer glass with high electrical conductivity

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Solid-state conducting polymers usually have highly conjugated macromolecular backbones and require intentional doping in order to achieve high electrical conductivities. Conversely, single-component, charge-neutral macromolecules could be synthetically simpler and have improved processibility and ambient stability. We show that poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl), a nonconjugated radical polymer with a subambient glass transition temperature, underwent rapid solid-state charge transfer reactions and had an electrical conductivity of up to 28 siemens per meter over channel lengths up to 0.6 micrometers. The charge transport through the radical polymer film was enabled with thermal annealing at 80°C, which allowed for the formation of a percolating network of open-shell sites in electronic communication with one another. The electrical conductivity was not enhanced by intentional doping, and thin films of this material showed high optical transparency.

Conducting polymers have relied on conjugated macromolecular backbones that are subsequently chemically doped so as to achieve high electrical conductivity values [for example, poly(3,4-ethylene dioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS)] (1, 2). Despite their impressive electrical conductivity values (3, 4), certain aspects of these macromolecules are not ideal. First, for some applications, optical transparency at visible wavelengths can be difficult to achieve with extended conjugated backbones. Second, the syntheses of advanced conducting polymers can be quite complicated with low yields. Third, chemical doping can depend on processing and lead to performance variability, and the dopants can decrease the materials and device stability.

Charge-neutral macromolecules that achieve relatively high electrical conductivity values without doping could address some of these issues (5). Radical polymers (6) with nonconjugated backbones and stable open-shell pendant groups (7, 8) can pass charge through a series of oxidation-reduction (redox) reactions between the pendant open-shell sites (9). Because of the high density of redox-active sites associated with these materials, they have had an effect on myriad energy storage and energy conversion applications (10–14). However, the highest solid-state electrical conductivity value reported for radical polymers was ~10−2 S m−1 (15).

Despite the low reported conductivity values, the redox reactions that allow for charge exchange between the pendant groups are rapid (16–18), so high conductivities should be possible with appropriate molecular engineering of charge-transporting sites (19). We synthesized poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl) (PTEO) using a ring-opening polymerization methodology, which allowed all of the radical sites in the monomer to be conserved in the polymer. Given its flexible macromolecular backbone and a near–room temperature glass transition temperature (Tg), its flow temperature is well below the degradation temperature of the macromolecule. Thermal annealing of the radical polymer thin film resulted in the formation of percolating networks of radical sites in the solid state that were in electronic communication with one another. This network formation occurred despite the amorphous nature of the polymer thin film. We achieved a >1000-fold increase in the electrical conductivity of PTEO relative to other report values for radical polymers, and the ultimate conductivity of ~20 S m−1 is comparable with commercially available, chemically doped conducting polymers.

We polymerized a monomer that contained an open-shell site directly because postpolymerization conversion of closed-shell pendant groups to open-shell forms rarely achieves complete conversion and can lead to undesired by-products (20, 21). We introduced a nitroxide functionality by reacting epichlorohydrin with 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO-OH) in the presence of a base (Fig. 1A). This small molecule, 4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (GTEMPO), was purified (fig. S1) in order to yield a well-defined monomeric species (22) that was stable across a range of different temperatures.

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Fig. 1. Controlling and monitoring the amount of open-shell sites in radical polymers is a key objective in the design of high-conductivity open-shell macromolecular species. (A) The monomer synthesis and ring-opening polymerization-based synthetic scheme used to generate the PTEO radical polymer. (B) The constant radical density (there is an overlapping nature of the spectra acquired at different temperatures) of the PTEO macromolecule in chloroform solutions as a function of temperature, as determined with EPR spectroscopy. (Inset) A photograph of the recrystallized monomer. (C) The EPR spectroscopy signal of a radical polymer thin film showing a classic Lorentzian shape, which is indicative of substantial radical-radical interactions in the solid state. (D) The ATR-FTIR spectra of the oxoammonium-based TEMPOnium salt, the GTEMPO monomer, and the PTEO polymer, indicating the absence of the oxoammonium cation signal in either the monomer or radical polymer used in this work.
interactions revealed multiple favorable pairing of the orientational dependence of TEMPO density functional theory (DFT) characterization between neighboring chains in a thin film. A PTEO, the main nitroxide interactions would be For this relatively low molecular weight of (or other dopant) sites present at lower levels. state that there are no oxoammonium cation ~0.1% (by weight) level, we cannot definitely data suggest that no dopants are present in the pants at the levels that can affect charge transport.

The glass transition temperature at ~20°C for the PTEO macromolecule is clear, and there is no melting or crystallization transition. (B) The onset degradation temperature of PTEO is ~150°C. (C) No degradation of PTEO was observed when the material was held at 80°C for 2 hours. (D) Percolation behavior as a function of radical density and annealing summarized from the Monte Carlo simulations. The average values are shown as solid lines, and standard deviations are shown as the shaded regions. (E and F) Typical configurations for the (E) unannealed and (F) annealed films at a radical density of 2.5 × 10^21 cm^-3. Independent networks are drawn with different colors, and any networks composed of less than five molecules are rendered gray and transparent. For example, in (F) almost all of the nitroxide groups are colored navy blue, indicating that there is one large continuous percolation network for charge transport after annealing has occurred.

High electrical conductivity requires a relatively low \( T_g \) so that the material can be annealed in the molten state and away from the degradation temperature of the radical pendant groups. The bulky nitroxide-containing substituent of the PTEO prevented crystallization of the polymer chains (fig. S4) and resulted in a \( T_g \) of ~20°C (Fig. 2A), which is well below the ~150°C onset of degradation for PTEO (Fig. 2B).

Thermal processing below 100°C (Fig. 2C) allowed us to create percolating nitroxide networks for charge transport between electrodes, which has not been seen for other systems because of the high \( T_g \) of most radical polymers, and this inability to process radical polymer thin films appropriately has contributed to reports of extremely low electrical conductivity values for nitroxide-based radical polymers (27).

We modeled radical network formation in PTEO with Monte Carlo (MC) simulations of the annealing process using a Hamiltonian parameterized with DFT calculations and with an implicit treatment of the polymer (supplementary materials). The configurations were then processed to characterize the radical networks and their degree of percolation (\( \beta \)) according to

\[
\beta = \frac{1}{3}(s_x + s_y + s_z)
\]

Here, \( s_i \) is the span of the largest network in each lattice dimension, with \( \beta \) ranging from 0 (no percolation) to 1 (complete percolation across the lattice). The simulations revealed a dramatic effect of annealing on the percolation behavior at all radical densities. Random distributions of the radical groups (an amorphous as-cast film) did not form percolating networks (Fig. 2D). Only after annealing did discontinuous subnetworks (Fig. 2E) combine through aggregation to form percolating networks (Fig. 2F). Moreover, only above a critical radical density could percolating networks form at all.

We monitored this transition for PTEO from the low-charge-transport regime (\( 10^{-9} \text{ S m}^{-1} \)) to the high-charge-transport regime (\( 10^{-6} \text{ S m}^{-1} \)) in real time as the material crossed from the as-spin-coated glassy state (the thin film was cast at ~20°C) into a liquid-like molten state (Fig. 3A).

In order to evaluate charge transport in this quenched state, the films were transferred to an inert atmosphere vacuum probe station and held at a temperature of 100 K. Heating of the sample occurred inside of the inert atmosphere.
Fig. 3. PTEO conducts charge after annealing has occurred. (A) Electrical conductivity as a function of temperature for PTEO in a 0.5-μm channel. Real-time annealing of the thin film allowed for local order to appear within the film so that the electrical conductivity was altered by 10 decades. (B) Above the glass transition temperature, there is thermally activated transport, whereas (C) below the glass transition temperature, the electrical conductivity is temperature-independent. The data points represent the average value measured for four different PTEO films, and the error bars represent the standard deviation from this average. If no error bars are present, the error is within the size of the point.

Fig. 4. The charge transport behavior of radical polymers is dictated by percolating domains of paired nitroxide groups. (A) Fragility analysis performed on the annealed networks as a function of radical density and defect density. (B) The electrical conductivity at \(T = 350\, \text{K}\) for PTEO as a function of channel length (black squares) shows that these localized domains were less than or equal to 600 nm in size in experimental practice. The data points represent the average of the measurements conducted on four different devices of that channel length, and the error bars represent 1 standard deviation from this average. If no error bar is shown, the error is within the size of the point. Equivalent experiments were performed with PEDOT:PSS (red squares) serving as the channel material, and there is almost no dependence on the conductivity as a function of channel length. (Inset) A scanning electron microscopy image of a typical channel used in these studies, showing the spacing between the gold electrode contacts before film deposition.

polymers (29), so our PTEO films should be strongly sensitive to the levels of defect incorporation and film processing. Over long enough length scales, defects will render the networks nonpercolative. Given the length scale limitations of our simulations, we can place a lower limit for the percolation length scale of \(\sim 20\, \text{nm}\) for radical densities greater than \(1.75 \times 10^{21}\, \text{cm}^{-3}\). The lack of crystallinity in these amorphous conductors made it difficult to experimentally determine the length scale at which the percolation of nitroxide groups ended. We estimated the size of high-charge-transport domains by changing the lengths between the two electrodes (Fig. 4B). At channel lengths \(>0.7\, \mu\text{m}\), the conductivity was low, \(\sim 10^{-4}\, \text{S m}^{-1}\) (21, 26). However, for channel lengths of \(0.6\, \mu\text{m}\) or less, the conductivity reached \(\sim 20\, \text{S m}^{-1}\). These data suggest that the nitroxide percolation network had a characteristic length scale of \(\sim 600\, \text{nm}\). Thus, if the high-charge-transport domains do not bridge across the electrodes, the conductivity is limited by the low-charge-transport domains. Bare channels and those containing polystyrene (PS) were fabricated and had conductivities below the detection limit (\(<10^{-12}\, \text{S cm}^{-1}\)) of our system (fig. S6). Similar experiments performed with PEDOT:PSS showed some contact resistance but otherwise exhibited high conductivity across this length-scale range, as expected, and the variation of its higher electrical conductivity for the same channel lengths was only twofold (Fig. 4B).

We evaluated how the chemical nature of the thin films affected the observed transport behavior. When the radical group within the PTEO repeat unit was intentionally quenched to form vacuum probe station in order to capture the charge transport ability at low temperatures before bringing the PTEO thin films near \(T_g\), so the changes in conductivity appear to be caused by changes in the nanoscale structure as opposed to changes in chemical oxidation. In these experiments, the sample was allowed to reach the desired temperature and held at that temperature for 30 min before collecting the electrical data. Then, the temperature of the sample was moved to the next temperature. Moreover, in a separate experiment, replicate devices were annealed at \(80\, ^\circ\text{C}\) for 2 hours in inert atmosphere conditions but without evaluating their low-temperature electrical properties (without the “1st heating” scan in Fig. 3A), and the conductivity of thin films processed in this manner began and remained at \(\sim 10\, \text{S m}^{-1}\) (in the same manner seen for the “2nd heating” scan of Fig. 3A), indicating that ordering was occurring though thermal annealing (fig. S5).

Once local order was created within the melt, it was retained as the thin film was cooled back into the glassy state, and this enabled rapid charge transport at room temperature both for cooling (Fig. 3A, red squares) and heating (Fig. 3A, blue triangles) of the thin film. Above \(T_g\), thin films displayed thermally activated transport with an activation energy of \(~90\, \text{meV}\) (Fig. 3B), which is consistent with the increased molecular motion. Moreover, as has been observed with other radical polymers (22, 26, 28), the transport was independent of temperature below \(T_g\) (Fig. 3C).

To study the role of defects, such as impurities or traps, we performed a fragility analysis on the annealed MC networks by removing a random distribution of the TEMPO sites from the annealed MC networks (those shown in Fig. 2, D to F) and recalculating the percolation behavior (Fig. 4A). Defect introduction has adverse effects at all TEMPO densities but was most sensitive near a TEMPO density of \(\sim 1.7 \times 10^{21}\, \text{cm}^{-3}\). We estimate that the TEMPO number density in PTEO is at least \(1.75 \times 10^{21}\, \text{cm}^{-3}\), on the basis of previous characterizations of chemically similar polymeric systems (24, 27).
the N-OH functionality (PTEO-OH), the electrical conductivity for the 0.5-μm channel decreased to ~10^{-7} S m^{-1} (fig. S7A). In order to form an electron donor-acceptor system within the radical polymer thin film, we intentionally doped the PTEO film with 4-acetamido2,2,6,6-tetramethyl-1-oxopiperidinium tetrafluoroborate (TEMPOnium) at a high loading (10%, by weight) (26). This intentional doping had little impact on the ultimate electrical conductivity of the film, and the conductivity showed the same marked increase after thermal annealing as was observed for the undoped system (fig. S7B). Moreover, making composite blends of PTEO and PTEO-OH at channel lengths of 0.5 μm allowed for experimental verification of the computational fragility analyses shown in Fig. 4A. That is, for thin films that contained >90% (by weight) PTEO, the electrical conductivity was ~10 S m^{-1}, as expected; however, when >20% (by weight) of the polymer composite was composed of inactive PTEO-OH, the conductivity of the thin film fell to ~10^{-5} S m^{-1} (fig. S7C). Thus, charge exchange from the injecting electrode to the collecting electrode depends on the ability of the nitroxide groups to form a percolating structure and not on any inherent limitations of the radical self-exchange reactions.

Last, the nonconjugated nature of the radical polymers led to weak absorption spectra of the material both in solution and as thin films. That is, the solution absorption spectrum showed the characteristic absorption signal for nitroxide-based radical polymers (fig. S8). However, the ~1-μm-thick PTEO film showed only minimal absorption in the visible spectrum, with ~98% transmission at wavelengths of λ ≤ 500 nm and 100% transmission at longer wavelengths. These thin films maintained their high electrical conductivity over multiple weeks (fig. S9) when they were exposed to ambient conditions. Thus, these radical polymer films present as relatively high-electrical-conductivity materials with high optical transparency and ambient stability.

**REFERENCES AND NOTES**


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**SUPPLEMENTARY MATERIALS**

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Materials and Methods
Figs. S1 to S9
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Moving charges with radicals
Conducting polymers usually contain backbones with multiple bonds. After chemical doping to remove some of the electrons, charge carriers can move freely. These conjugated backbones can also make the polymers rigid and hard to process. Joo et al. synthesized a redox-active, nonconjugated radical polymer that exhibited high conductivity (see the Perspective by Lutkenhaus). The polymer has a low glass transition temperature, allowing it to form intermolecular percolation networks for electrons.
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