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NITRO-STABILIZED PROTON ABSTRACTION DOPED MODEL
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UNIVERSITY PARK DEPT OF MATERIALS SCI..

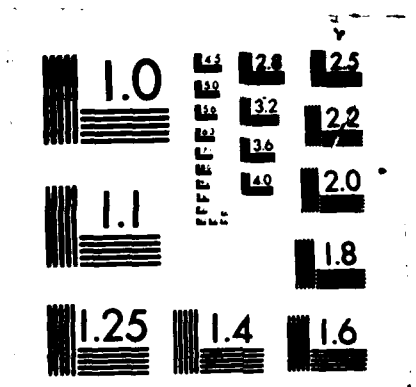
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Nitro-Stabilized Proton Abstraction Doped Model Compounds
As Precursors To Conducting Polymers

by

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nitro stabilized conductive anions offer much promise in overcoming many of the traditional problems plaguing the conductive polymer field.

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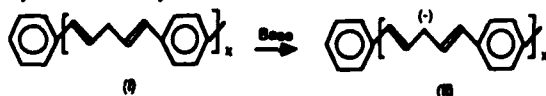


NITRO-STABILIZED PROTON ABSTRACTION DOPED MODEL COMPOUNDS AS PRECURSORS TO CONDUCTING POLYMERS

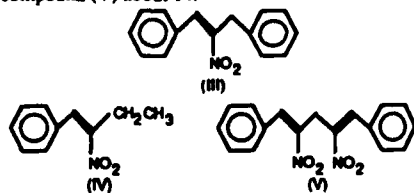
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Conducting polymers have gotten quite a bit of attention recently with potential future end uses in lightweight batteries, electromagnetic interference shielding, antistatic devices, and various space applications, but a few problems still exist that severely plague the field. Traditionally, these problems include the need for toxic dopants, the material intractabilities that hinder processing, and poor environmental and oxidative stabilities. Most work on solving these problems are based on electron transfer as a "doping" mechanism. In our laboratory, we have defined a new mechanism based on Proton Abstraction Doping (PAD),¹ which has eliminated many of the above problems but has created several of its own. Our previous work has centered on abstraction of doubly benzylic and/or allylic protons with strong base, but both the use of strong base and the resulting reactive anion make this a difficult system to handle in the air.

This paper will outline one phase of our current work in making nitro-stabilized PAD conducting model compounds and other moieties for later incorporation into polymers in order to alleviate the above problems. The PAD technique of removing protons from doubly benzylic and/or allylic sites to obtain conductive anions has shown promise in our laboratory.² It also helps overcome the need for highly toxic dopants and even material intractability problems before doping. First, a base is used to abstract a proton to form a conducting anion instead of using a toxic reducing agent. Second, the precursor (i.e. I) contains an isolated methylene in each repeat unit that is free to rotate thus making the polymer soluble whereas the traditional totally-conjugated precursors are typically intractable. And third, in comparison to totally-conjugated precursors, PAD precursors are more likely to be oxidatively stable.

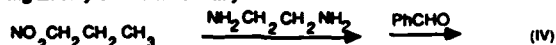


Another benefit of this proposed investigation lies in trying to increase environmental and oxidative stabilities of these model compounds. Since nitro groups (and other electron withdrawing groups) withdraw electron density from the proposed anions (such as VI), these materials are less likely to react with protic and electrophilic species in the environment than nonstabilized equivalents. Restating this, materials like (III), (IV), and (V) have quite lowered pKa's relative to equivalent materials without electron withdrawing groups. [Also a kinetic argument of Finkel'stein³ seems to show that these nitro materials may have increased oxidative stabilities for similar reasons.] Compound (III) has an estimated pKa of about 19 based on a simple extrapolation method using standard pKa tables.⁴ By this method, the pKa of compound (IV) is estimated to be 24, and that of compound (V) about 14.



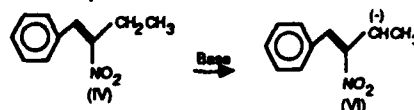
We decided to examine these low molecular weight model compounds since early work in our laboratory showed reasonable conductivities with such materials. Since these low molecular weight species are easier to prepare, purify, and characterize than their high molecular weight polymeric analogs, they make an ideal choice for conductivity studies.

The model compounds in this work have all been produced via Lerner's⁵ method of condensation of active hydrogens with aldehydes using an ethylenediamine catalyst.



Using this basis, compound (IV) was produced from benzaldehyde and nitropropane, compound (III) from 2-phenyl-1-nitroethane and benzaldehyde, and compound (V) from 1,3-dinitropropane and benzaldehyde. All were purified by either high pressure liquid chromatography or vacuum distillation directly prior to doping via PAD.

The same preparation, purification, and characterization benefits are seen with the anion PAD-produced species. They are prepared using a relatively weak base potassium *tert*-butoxide as shown below:



Preliminary conductivity tests show steady readings of about 10^{-7} (cm Ω^{-1}) in air for anion salt (VI). The measurements were constant over each of the five days tested. Longer time-scale tests will be run with results to follow. Although these conductivities are a few orders of magnitude lower than previous readings we have taken, they offer much promise. The lower readings are attributed to a "localized" anionic species nature that does not allow for the aromatic ring to be delocalized into the pi network. Future efforts will examine means of forcing the aromatic ring into the stabilized, delocalized, conductive, anionic network and should thus have higher conductivities similar to those we have seen before. These will then be incorporated into a polymer backbone or attached to a polymer as a pendant side group to produce a stabilized conductive polymeric system.

In conclusion, this work has shown that PAD is one good alternative method to the oft-problematic current methods of producing stable, conveniently-useful conductive polymers. The PAD technique eliminates the need for highly toxic dopants and uses materials that are less intractable before doping, but produces a few problems of its own such as material stability in air. With the incorporation of electron withdrawing groups such as nitro groups into these materials, this problem seems to be overcome as evidenced by the five-day constant conductivity finding. The current preliminary results show that much work is still necessary, but PAD nitro stabilized conductive anions offer much promise in overcoming many of the traditional problems plaguing the conductive polymer field.

ACKNOWLEDGEMENT: The support of the Office Of Naval Research is gratefully acknowledged.

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