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New Anode- and Cathode-active materials for Organic Batteries

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“We give advice, but we cannot give the wisdom to profit by it”

François de La Rochefoucauld

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T. Jähnert,[1] B. Häupler,[2] T. Janoschka,[3] M. D. Hager,[4] U. S. Schubert,[5] *Macromol. Chem. Phys.* **2013**, *214*, 2616–2623.

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T. Jähnert,[1] M. D. Hager,[2] U. S. Schubert,[3] *Macromol. Rapid Commun.* **2016**, *37*, 725–730.

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Name Erstbetreuer(in)	Datum	Ort	Unterschrift

1 Introduction

Today, commercial batteries are usually fabricated with metals, metal oxides or intercalated metal compounds. In these battery types polymers are mostly only used as electrolytes or as casing.[1,2] Electro-active polymers were not widely considered as electrode materials until the turn of the century. With the publication of Nakahara *et al.* in 2002 a new type of battery was born.[3] These organic radical batteries (ORBs) have seen a rapidly growing interest in recent years. Many groups around the world are now trying to develop new polymeric materials and to improve existing ones to turn ORBs into a competitive alternative to metal-containing battery systems.[1-4]

In 2002 Nakahara *et al.* published an article proposing the use of a polymer with stable radicals as pendant groups for the use in batteries. The applied polymer poly(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl methacrylate) (PTMA) was a poly(methacrylate) functionalized with TEMPO.[5] TEMPO and other nitroxide-radicals were used before in one-dimensional organic ferromagnets or as mediators in controlled nitroxide mediated radical polymerization processes.[1, 6, 7] In ORBs, however, these radicals were not used due to their magnetic properties or their ability to reversibly react with other radicals, but due to their reversible redox-reaction. The nitroxide-radical can be reversibly oxidized to its cationic form, the oxammonium cation. This enables nitroxides to be used as cathode-materials in ORBs.[1, 2] Of course not all nitroxides can be used. The stability of the nitroxide is determined by the substituents on the nitrogen.[8] Quarternary carbon-based substituents like, *e.g.*, in *di*-tert-butyl-nitroxide or TEMPO, make the compounds very robust, whereas substituents like hydrogen in α-position open up decomposition-pathways.[9, 10] The prime example for stable nitroxides in ORBs is TEMPO.[2] This nitroxide has been incorporated into several polymeric structures, *e.g.*, poly(methacrylate)s,[5] poly(acrylate)s,[11] poly(vinylether)s,[12] poly(styrene),[13] poly(acrylamide),[14] poly(norbornene)s[15] and poly(siloxane)s.[16] They possess the ability to be charged very fast and show a good capacity as well as stability over hundreds or thousands or charge-discharge cycles.[1, 2, 14] With this incredible performance ORBs were determined to be environmental friendly (no metals), simply processable (screen- or inkjet-printing) and possessing high power density (charging in seconds possible) and excellent cycle-life (>1000 charging/discharging cycles).[1, 2, 5] Apart from TEMPO other nitroxide-structures were also tested for battery-applications (**Figure 1-1**). The main goal of many investigations was the adjustment of the redox-potential by introduction of substituents, *e.g.*, phenyl or trifluoromethyl as well as the increasing of the materials theoretical capacity by decreasing the molar mass per redox-active unit.[2, 13, 17, 18]

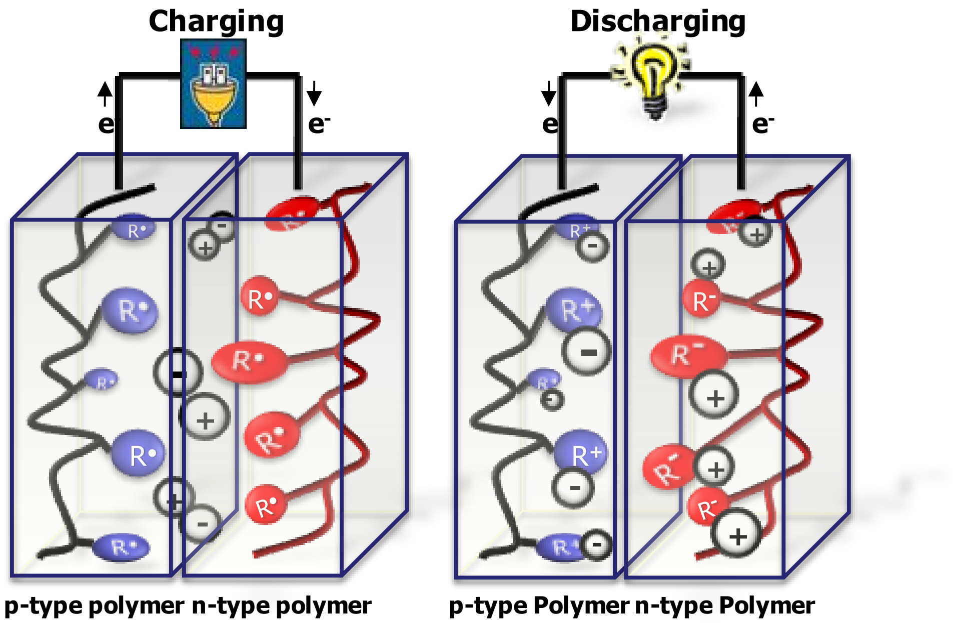


Figure 1-1: Schematic representation of an all-organic battery.

Nitronyl-nitroxides[19] and BODIPY-containing polymers belong to a small group of compounds that are able to function as cathode as well as anode material. This advantage can be used in all-organic batteries consisting of only one polymeric compound, which is used as active material for both electrodes.[1,2] Apart from using these polymers as anode material several dedicated anode materials have been developed and investigated for their properties as electrode material in ORBs. Galvinoxyl-radicals possess a very good stability and were therefore investigated as anode-materials.[15, 20] Before their application in ORBs they were used as radical-standards, for magnetic investigations or as radical-scavengers.[21] Polymeric galvinoxyls were reported with styrene,[15, 20] aryleneethynylene[22] or phenylethynylene[21] as backbone. The most investigated of all those is the poly(vinylphenyl)galvinoxyl.[15, 20] This polymer has been tested in batteries with lithium, where a capacity of 42 mAh/g was held for 500 cycles.[15] In all-organic batteries with TEMPO-substituted poly(norbornene) 250 charge-discharge cycles could be measured[15] and in another battery with a poly(nitronylnitroxylstyrene) charging-capacities up to 150C were tested with only a slight loss in overall capacity of the system.[19] Phenoxyl-radicals can be considered as a smaller form of the galvinoxyl-radicals. They are less frequently used than galvinoxyl, because they are often less stable. However, the much higher theoretical capacity makes them a worthwhile research topic.[23] Phenoxyl-radicals have also been incorporated into polymers, as poly(thiophene)s,[24] poly(styrene)s,[25] poly(methacrylate)s or poly(norbornene)s.[23] Due to being less stable than their galvinoxyl-counterparts only 100 charging-discharging cycles have been accomplished in literature so far. To even achieve stable phenolic radicals bulky functional groups have to be introduced near the radical center.[23] Computational studies have shown that the oxygen-atom in phenoxyl-radicals possess only a marginally higher spin-density than the *ortho*- and *para*-carbons. In galvinoxyl-radicals there is also substantial spin-density on the *para*-carbons.[26] To block these positions from further undesired reactions substituents like *tert*-butyl are introduced to stabilize the molecules. These radicals also often need a basic environment to function properly.[23, 26] The challenge is to identify the best polymer – most stable, highest capacity, easiest synthesis, cheapest materials – and to adapt the electrolyte and electrode to the system to achieve a maximum performance. Several systems have been described in literature using TEMPO,[5, 11-16] galvinoxyl[15, 20] or viologene[14] as electroactive groups but none have been commercialized so far.

The goal of this thesis was to develop new polymers as active battery-materials and test their capabilities in batteries. This includes the functionalization and optimization of well-known polymers like galvinoxyles and the incorporation of less-known redox-materials in polymeric compounds. Several new polymers, containing anode- or cathode-active compounds were synthesized. Galvinoxyl- and phenoxyl-compounds are addressed in chapter 3. Quinones, anthraquinones and nitroxides are the topic of chapter 4. These polymeric compounds were subsequently intensively tested for their application as electrode material and incorporated into batteries, including the fabrication of a battery using inkjet-printing in chapter 5. By changing the functional groups of the polymers, their redox-potentials, stability or solubility are changed and new batteries were created. Those different batteries show the versatility of polymers as electrode-materials and the possibility to adjust a batteries capability to the desired specifications.

2 Phenolic radicals as antioxidants, battery materials or in metal complexes

Parts of this chapter have been published: P7) T. Jähnert, M. D. Hager, U. S. Schubert, *J. Mater. Chem. A* **2014**, 2, 15234–15251.

Phenolic radicals are all radicals generated from phenolic structures. Often they are also described as phenoxyl-radicals. Some of these radicals are only stable for milliseconds, while others can be kept almost indefinitely.[15, 20] Depending on these and other characteristics a variety of applications for phenolic radicals has been investigated. They can be used as antioxidants and radical scavengers,[27, 28] in hydrogen-bonding experiments,[29] as magnetic materials,[22] in organic batteries[15, 20] and in metal complexes (**Figure 2-1**).[30] They can also often be found in plants or animals, where they can be created during biological processes or as reaction to some kind of stimulus, *e.g.,* ionizing radiation.[31] Like other radicals phenolic radicals possess an unpaired electron. In phenolic radicals this is usually delocalized over the aromatic rings and its substituents. This leads to several highly reactive positions in the molecule. Pathways, in which these positions can react, include dimerization, disproportionation, hydrogen-abstraction or addition-reactions (**Scheme 2-1**).[26, 30] To circumvent such reactions bulky substituents in *ortho*- and *para*-positions are introduced.[23] In this way stable phenoxyl-radicals like the 2,4,6-tri-*tert*-butylphenoxyl can be created, which is often used as experimental standard.[26, 30] The initial creation of phenoxyl-radicals can be accomplished by chemical oxidation with compounds like PbO_2 or $K_3[Fe(CN)_6]$, laser photolysis, ionizing radiation or radical-abstraction from other radicals like the hydroxyl-radical.[21, 23, 31] In biological systems antioxidant activity and radical scavenging are the main applications for phenolic radicals.[27, 32] Here they can react and neutralize highly reacted radicals generated by ionizing radiation.

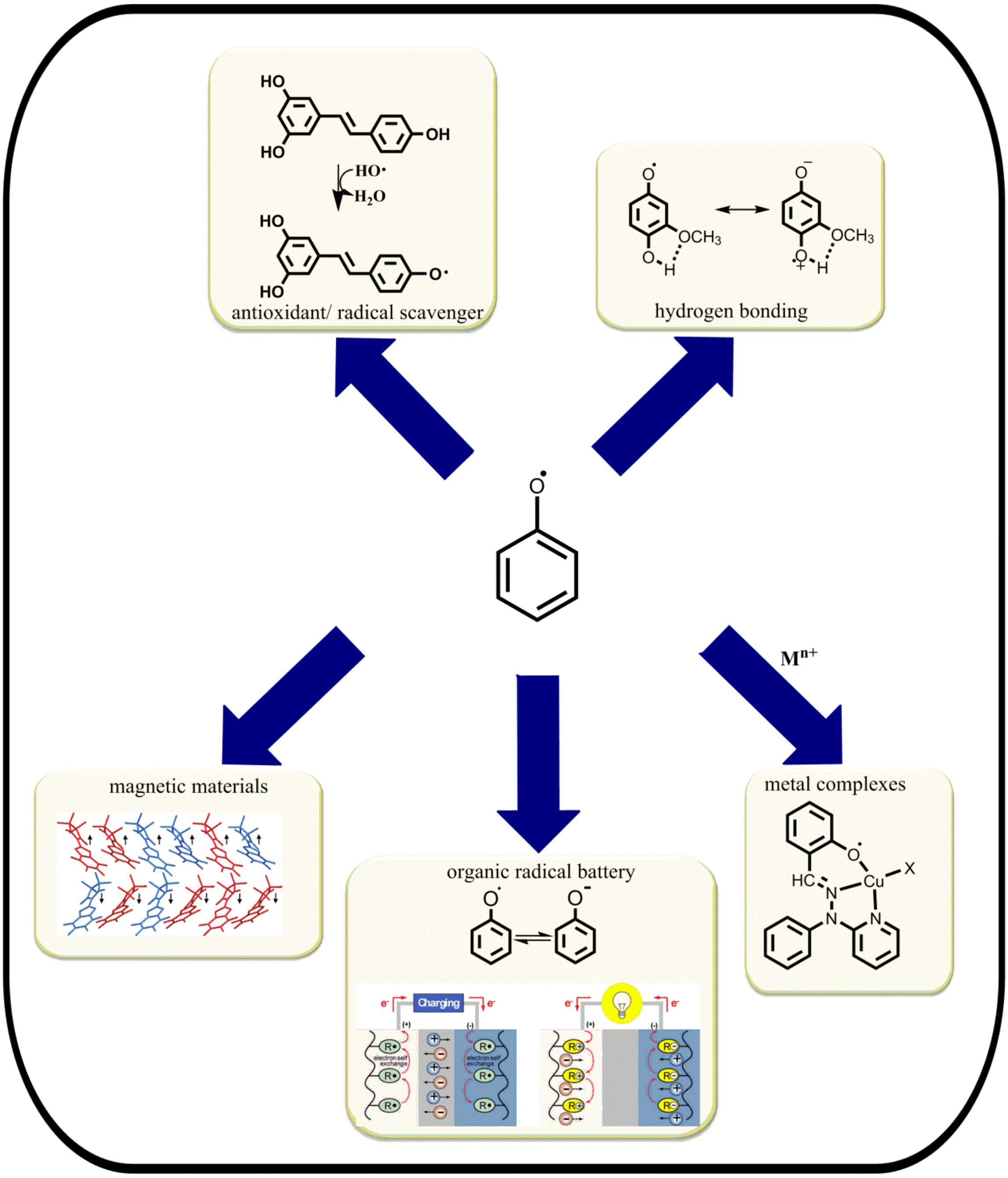
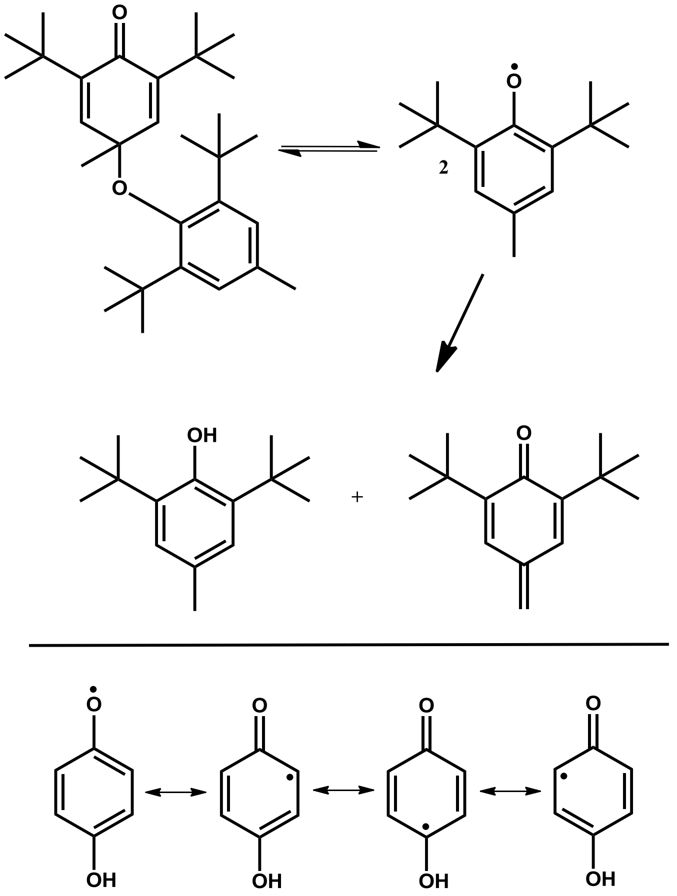


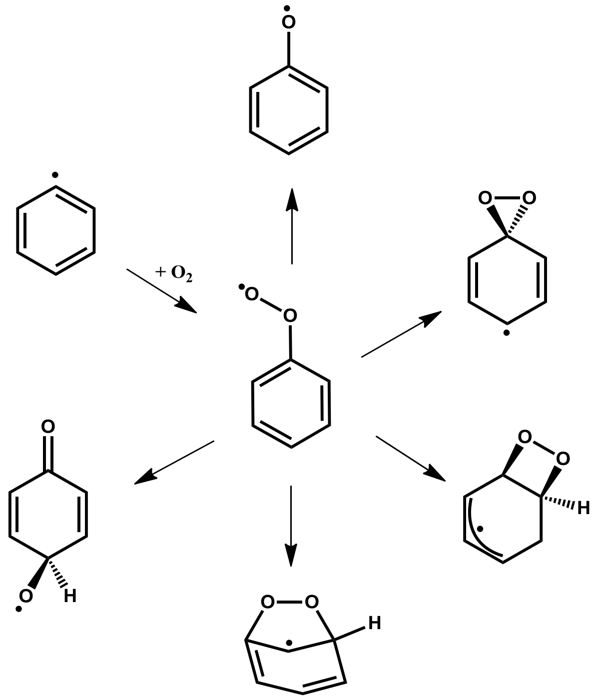
Figure 2-1. Uses of phenolic radicals as antioxidant/radical scavenger, for hydrogen bonding, magnetic materials, organic radical batteries and in metal complexes.

These include hydroxyl-, peroxide- or azide-radicals as well as oxide radical anions.[32] The so formed phenoxyl-radicals usually dimerize shortly after their generation unless its substitution-patterns stabilizes the radicals.[26, 30, 32] In phenoxyl-radicals with conjugated heterocyclic rings as substituents in *para*-position, the spin-density of the whole molecule can be delocalized, thereby moving the major spin-density away from the phenoxyl-radical center.[33]



Scheme 2-1. Schematic representation of the dimerization or dissociation of the 2,6-di-*tert*-butyl-4-methylphenoxyl radical (top) and the delocalization of the radical in the *p*-hydroxyphenoxyl radical system (bottom).

Phenolic radicals have been investigated for a long period of time due to their interesting properties. These compounds have found applications, *e.g.*, in biology. They have also been investigated experimentally as well as theoretically, but to understand their abilities their basic chemical structures have to be discussed. Most phenolic radicals are based on the phenoxyl-radical. Phenoxyl-radicals are usually obtained by oxidation of the corresponding phenols.[21, 23, 31] These radicals are most often investigated to understand the formation of the radicals, the underlying reaction mechanism and the influence of the substituents during the radical formation and on their stability. Incorporated into conjugated polymers like polythiophene[34] and poly(isonaphthene methine)[35] they have gained interest because of their low band-gap value, high spin-concentration[35] and magnetic properties.[34] Another radical is the phenylperoxyl-radical. This can be created by reaction of phenyl radicals with oxygen. These simple radicals can decompose in different pathways. They can, *e.g.*, decompose to phenoxyl-radicals or cyclopentadienyl-radicals (**Scheme 2-2**).[37] Phenylperoxyl-radicals are part of combustion-processes, play a role in the oxidation of volatile compounds in the atmosphere and in cellular lipid oxidation as well as can damage DNA.[37] During combustion of aromatic hydrocarbons the formation of these radicals, by the reaction of phenyl-radical and oxygen, can contribute to the formation of ozone.[38] It is also believed that during combustion phenylperoxyl-radicals are the primary intermediates of all degradation-products of aromatic hydrocarbons.[39] As with phenoxyl-radicals the reactivity of these radicals is influenced by their substitution-patterns. Electron-withdrawing substituents in *para*-position to the radical can increase the rate constant for oxidation by the radical and electron-donating substituents can decrease it.[40]



Scheme 2-2. Schematic representation of decomposition-paths of the phenylperoxyl-radical.

The research on naphthoxyl-radicals is focused on health, because they are intermediates in the dissociation of nitrated aromatic hydrocarbons emitted during combustion. These substances can be carcinogenic and mutagenic.[41] The most unique phenolic radical is the galvinoxyl-radical. It is also the most frequently investigated phenolic radical, because of its excellent stability and almost complete inertness to oxygen.[15, 20-22] The structure of the galvinoxyl-radical is similar to the triphenylmethlyl-radical. It possesses a single radical-center, which can be delocalized between the two oxygens.[26] A diradical, the Yangs biradical, also exists, which revealed that most of the molecules spin-density is located on the carbons adjacent to the center carbon.[30] The stability of the radical is due to the delocalization of the unpaired electron and the bulky *tert*-butyl substituents.[26]

The most common and probably most important use of phenolic radicals is as antioxidant and radical scavenger. Many reactive oxygen species, generated by ionizing radiation, are involved in pathological conditions like aging as well as cancer and their effects can be diminished or contained by the antioxidants found in many fruits, *e.g.,* by resveratrol[42] and tocopherol.[43] Resveratrol is one of the most frequently studied phenolic antioxidants. Due to its phenolic structure it can react with highly reactive radicals and form a phenoxyl-radical in the process. This radical, however, is not stable indefinitely and dimerizes quickly to a dihydrofuran dimer.[44] The overall efficiency of radical-scavenging depends on the bond-dissociation-enthalpy of the hydroxyl-group. Several stilbene-analogues and substituted resveratrol-compounds have been investigated and it has been discovered that electron-donors increase and electron-withdrawing groups decrease the radical-scavenging activity.[44, 45] Similar results have been found in the radical-scavenging behavior of acetylsalicylic acid and paracetamol. It has been discovered that, in these molecules, electron-withdrawing groups destabilize the radicals, while electron-donors stabilize them. The number of hydroxyl-groups can also increase the scavenging activity.[46] Other prominent radical-scavenging phenols, which are also often used as reference-substances, are tocopherol[43] and its analogue trolox.[47] α-Tocopherol, as the most abundant and active form of vitamin E, has a large role in tissue cells and acts as antioxidant to prevent living cell membranes from decomposing.[43] Apart from most other naturally occurring phenolic radicals tocopherol-radicals are relatively stable due to the two methyl-groups in *ortho*-position to the radical-center.[48] Several different phenolic compounds can also act as radical scavengers. Among those are chalcones,[49] flavonoides[50] and tannins.[51] During the process of radical scavenging they form the corresponding phenoxyl-radicals. Although these may not be stable, depending on the substitution-pattern, they are less harmful compared to peroxyl- or hydroxyl-radicals. Some of these substances were investigated for their use in biological systems as drugs or dietary supplements.[52, 53]

Hydrogen-bonding is not only observed for closed-shell systems, but also for radical moieties.[29] Such open-shell hydrogen-bonds can often be found in enzymatic systems.[54] Tests with model-compounds have shown that phenoxyl-radicals can be part of oxygen-insertion reactions by cytochrom P450.[55] Phenolic compounds act here as hydrogen-radical donor. Phenoxyl-radicals can form intermolecular and intramolecular hydrogen-bonds. Intermolecular hydrogen-bonding between phenols and solvent molecules have been shown to reduce the ability to donate hydrogen-radicals to other radicals.[56-60] Hydrogen-bonding can also influence the redox-potential of the reversible reaction between the phenoxyl-radical and the phenolate-anion.[57] Another characteristic of phenoxyl-radicals are their magnetic properties. In the solid state these are determined by intermolecular and intramolecular interactions, which depend on the crystal structure. Thus it is possible to tune the magnetic properties by changing the crystallographic packing. In short range-assembled crystals, crystal geometries might be predicted, but general predictions of magnetic properties based on the molecules structure are not possible.[61] Even small changes in the molecular structure can have great influences on magnetic properties. In diradicals the magnetic properties are even more difficult to quantify. The interaction of unpaired electrons connected through aromatic moieties can be adjusted to switch between antiferromagnetic and ferromagnetic behavior.[62]

The electrochemical properties of phenolic radicals have also been studied extensively, even more so after the development of organic radical batteries.[5] In ORBs phenolic radicals can be used as anode-active materials to store energy. In this case the phenoxyl-radicals can be reduced to their anionic form and reoxidized to the radical possibly hundreds of times.[23, 26] The research on ORBs mainly focuses on cathode-materials based on nitroxide-radicals, in particular TEMPO-substituted polymers. The research on anode-materials is less extensive as metals like zinc and lithium are often used as anode-materials in combination with nitroxide-polymers as cathode-materials.[1, 2] As one of the first polymeric anode-materials poly((vinylphenyl) galvinoxyl) was used. With a theoretical capacity of 51 mAh/g its capacity is low, but because of its extraordinary stability it is an often applied material. The radical is almost completely insensitive to oxygen, but to stabilize the anion a base like tetrabutylammonium hydroxide is often added.[15] Poly((vinylphenyl)galvinoxyl) has also been implemented in all-organic batteries with TEMPO-substituted norbornene[15] or poly(nitronylnitroxylstyrene).[19] With the TEMPO-substituted norbornene a stable capacity of 32 mAh/g over 250 cycles was achieved.[15] With poly(nitronylnitroxylstyrene) a charge-rate of 150 C was achieved with only minimal losses and with lithium as counter-electrode the system was stable for 500 cycles at 42 mAh/g for 500 cycles without loss.[19] Galvinoxyl-moieties have also been incorporated in other polymeric architectures such as polythiophene,[63] poly(phenylethynylene)[21] and in structures with binaphthol-groups.[64] With poly(phenylethynylene) as polymer-backbone galvinoxyl was even tested in an aqueous environment.[21] Other polymeric architectures were not yet used as electrode-materials for organic batteries. Phenoxyl-radicals have also been incorporated into polymers. As moieties in polythiophenes[63] and poly(phenylenevinylene) phenoxyl-radicals are investigated for their magnetic properties and considered as candidates for high-spin, electrically conductive polyradicals.[25] For ORBs they were investigated in poly(methacrylate)s and poly(norbornene)s. The phenoxyls perform reversible redox-reactions to their phenolate-form. This happens at a redox-potential of –0.6 V (*vs*. Ag/AgCl).[23] Tocopherol has also been tested for its electrochemical behavior. An electrochemical oxidation of α-tocopherol leads to the radical-cation. This dissociates to the radical and can subsequently be oxidized to the cation. The redox-potentials of tocopherol are dependent on the pH-value. Under neutral conditions a potential of 0.2 V, under acidic conditions of 0.5 V and under basic conditions of –0.8 V (all *vs.* Fc/Fc^+) can be achieved.[65] The redox-properties of other phenolic radicals have not been studied in detail yet.

Recently phenoxyl-radicals became quite prominent as parts of metal complexes, in particular metal complexes which can serve as models for the active center of enzymes. There phenoxyl-radicals often serve as co-factors for living organisms. Examples for such enzymes are galactose oxidase,[66] glyoxal oxidase or SCO2837p. In those enzymes a tyrosyl-radical is situated in the proteins active site and model complexes try to emulate this.[67] Galactose oxidase contains a copper-center and performs the oxidation of a primary alcohol to an aldehyde with oxygen, which is reduced to hydrogen peroxide.[66] To simulate this several copper-complexes were synthesized on this model, while trying to manipulate the optical and redox properties as well as studying the influence of the tyrosyl-radical on the enzyme.[68,69] Apart from the single-copper complexes dimeric complexes have also been explored. Peroxo-groups or chlorides can link the copper-ions in these complexes.[70, 71]

Complexes with phenoxyl-radicals and nickel as well as cobalt exist in both their +2 and +3 forms and were investigated in their radical form and their two-electron oxidized form.[71-75] Galvinoxyl has also been used as ligand in a cobalt-complex. This radical is very rarely used in metal-complexes, but yields stable compounds with cobalt-ions.[76] Apart from the aforementioned Cu-, Ni- and Co-complexes the other 3d-elements can also be found in phenoxyl-metal-complexes. Iron-complexes are part of prostaglandin-H-synthases, the R2 protein of ribonucleotide reductase and dioxygenase enzymes. In many of these systems oxidation of these complexes leads to the oxidation of phenolate to phenoxyl-radicals.[77] Mn-complexes were also considered as models for a ribunucleotide reductase R2 enzyme and their catalytic activity for epoxide ring-opening reactions.[78] Cr(II) and Zn(III) were seldom used in complexes with phenoxyl-radicals, but some examples exist for their use as models for the active center of enzymes. Some complexes of palladium are used for their catalytic activity, platinum-phenoxyl complexes are investigated for their luminescence and excellent quantum yield and dysprosium-phenoxyl complexes were created as single-molecule magnets.[79]

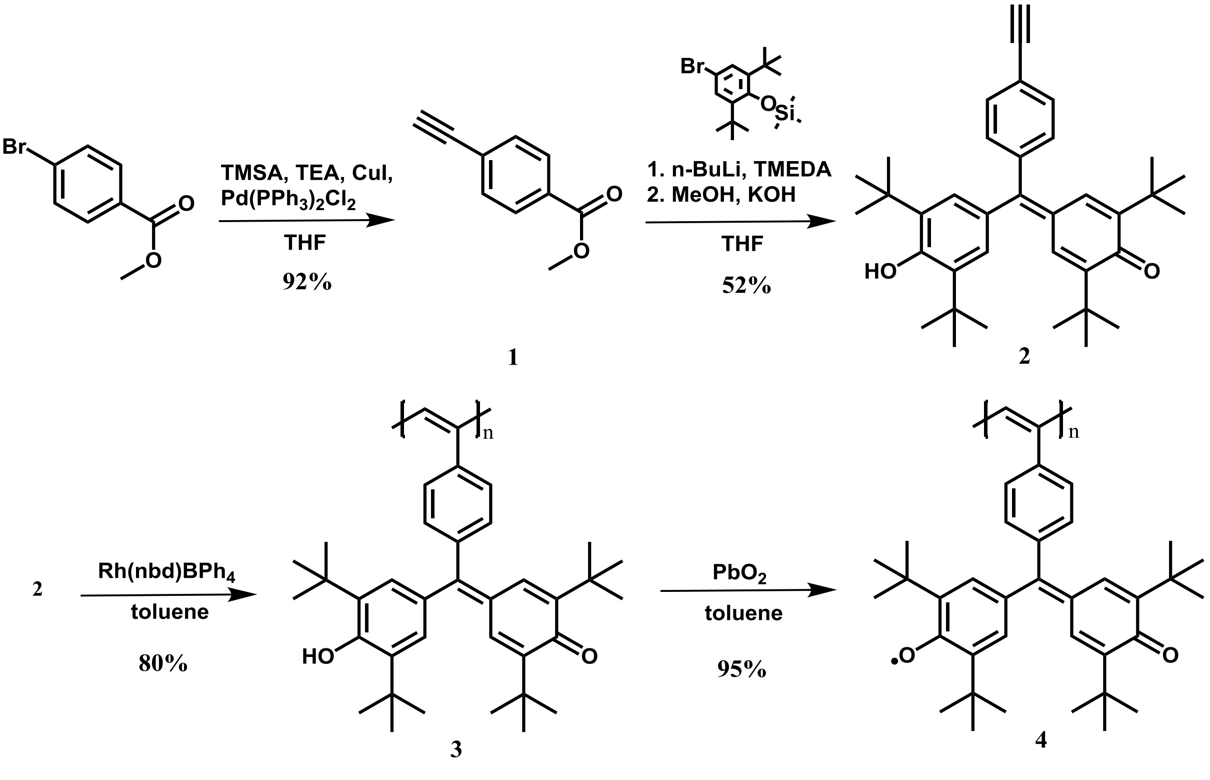
3 Anode-materials based on phenoxyl- and galvinoxyl-polymers and their use in aqueous systems and lithium-batteries

Parts of this chapter have been published: P1) T. Jähnert, B. Häupler, T. Janoschka, M. D. Hager, U. S. Schubert, *Macromol. Chem. Phys.* **2013**, *214*, 2616–2623; P2) T. Jähnert, B. Häupler, T. Janoschka, M. D. Hager, U. S. Schubert, *Macromol. Rapid Commun.* **2014***, 35,* 882–887; P7) T. Jähnert, M. D. Hager, U. S. Schubert, *J. Mater. Chem. A* **2014**, *2*, 15234–15251; P8) T. Jähnert, M. D. Hager, U. S. Schubert, **2016**, *37*, 725–730.

3.1. Synthesis of conjugated galvinoxyl-radical containing polymers, their electrochemical behavior and application in an all-organic radical battery

The development of new anode-materials for organic radical batteries has seen fewer publications than that of cathode-materials since the first publication about organic radical batteries by Nakahara *et al*. in 2002.[5] Research was so far largely focused on nitroxide-containing polymers like PTMA, PTVE and others. A reason for this is the already large library of available nitroxide-compounds.[1, 2] Many stable nitroxides were already used for nitroxide mediated polymerizations (NMP) and only had to be repurposed and integrated in a polymeric backbone. Another reason is that many nitroxides, in particular TEMPO, are insensitive to oxygen and water and work well under most pH-values.[26, 30] Anodic materials, on the other hand, are sparsely investigated. The most studied anode-material is still the galvinoxyl due to its stability and resistance against oxygen, although the reduced form is sensitive to oxygen.[15, 20] Other interesting anode-materials, which have been investigated, are quinones,[1] bipyridines[14] and phenoxyl-radicals.[23] Research on those compounds, however, is still in its infancy. If two different polymers are used the cell-voltage can be adjusted with different polymers, but the electrolyte has to be adjusted to work with both compounds. Both approaches possess advantages and disadvantages.

The research on galvinoxyl or phenoxyl in ORBs has been restricted to poly((vinylphenyl(galvinoxyl))[15, 20] and its application in different all-organic or metal-containing polymers. Conjugated polymers using polythiophene as backbone[63] have not been incorporated into organic batteries, but have only been used as magnetic materials. Other conjugated galvinoxyl-polymers using poly(phenylacetylene) as polymeric component were envisioned and synthesized. The synthesis of a galvinoxyl is usually performed with a silyl-protected 4-bromo-2,6-di-*tert*-butylphenol and a phenylester **1**. The later moiety is functionalized with the polymerizable group, which has to stand the reaction conditions (*n*-BuLi, basic conditions) of the coupling to the hydrogalvinoxyl-compound. By this manner (*p*-ethynylphenyl)hydrogalvinoxyl **2** (**Scheme 3-1**) as well as (3,5-diethynylphenyl) hydrogalvinoxyl were synthesized. Both hydrogalvinoxyl-compounds are sensitive to oxygen and can be oxidized in a matter of weeks. To avoid unwanted oxidation the monomers were polymerized shortly after synthesis. The polymerization of phenylacetylene-monomers in literature is performed with the help of rhodium-compounds as catalysts. Tests were performed using rhodium(bisnorbornadiene(tetrafluoroborate)) and rhodium (norbornadiene(tetraphenylborane)).



Scheme 3-1. Schematic representation of the synthesis of polymers **3** and **4**.

Both catalysts yield polymers, but the tetraphenylborane-substituted catalyst results in poly(galvinoxyl) **3** with higher molar masses. With the addition of triethylamine even higher molar masses can be obtained. After the polymerizations the polymers had to be oxidized to their radical-form **4**. This was done in solution using lead dioxide as oxidant. Firstly, the electrochemical properties were studied by cyclic voltammetry. In literature a redox-potential of 0.06 V *vs*. Ag/AgCl is described for poly(vinylphenylgalvinoxyl. The tested conjugated galvinoxyl-polymers showed redox-potentials at –0.40 V *vs.* Fc/Fc$^+$ (**Figure 3-1**), which fits well with the previously reported values. The conjugated polyphenylacetylene-backbone can also be seen in the CV as small signals next to the galvinoxyls. The polymers were subsequently tested for their charge-discharge capabilities in an aqueous electrolyte using sodium chloride as salt. The polymers achieved up to 60% of their theoretical capacity (**Figure 3-1**). With the radical content of the polymers determined *via* ESR to be about 70% and a theoretical error of about 10% of the ESR, these values are promising results for the first polymeric galvinoxyl-compound **4** in an aqueous electrolyte. Although the capacities fall about 10% after 40 cycles this system works well as a proof-of-concept for phenolic radicals as anode-materials for organic batteries in aqueous electrolytes. This was further shown by the incorporation of poly((*p*-phenylacetylene)galvinoxyl) **4** and PTMA into an all-organic radical battery. This system was successfully tested under neutral conditions with moderate capacities. A 0.1 M aqueous solution of NaCl was used as electrolyte for this test-cell. The battery revealed the expected charge-discharge behavior with charge-discharge potentials between 1.0 and 1.2 V.

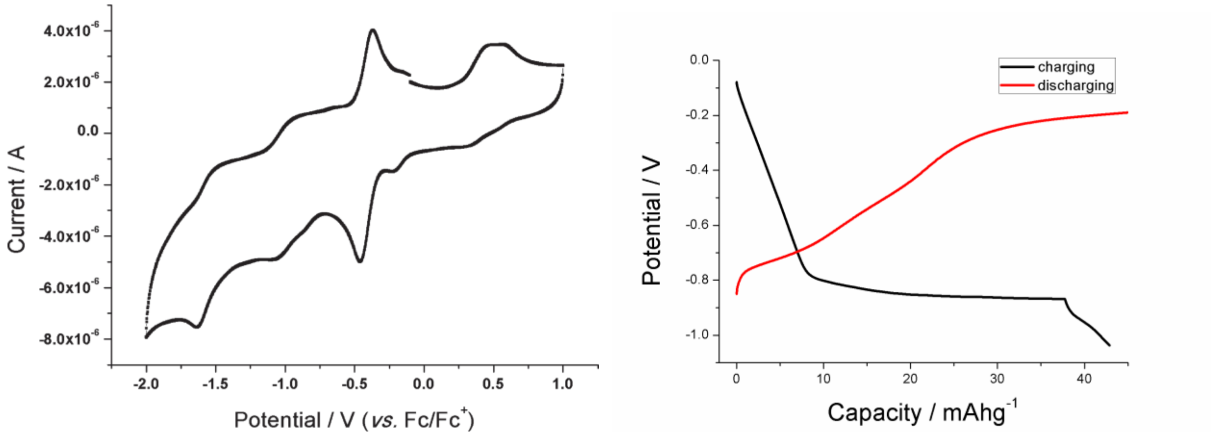
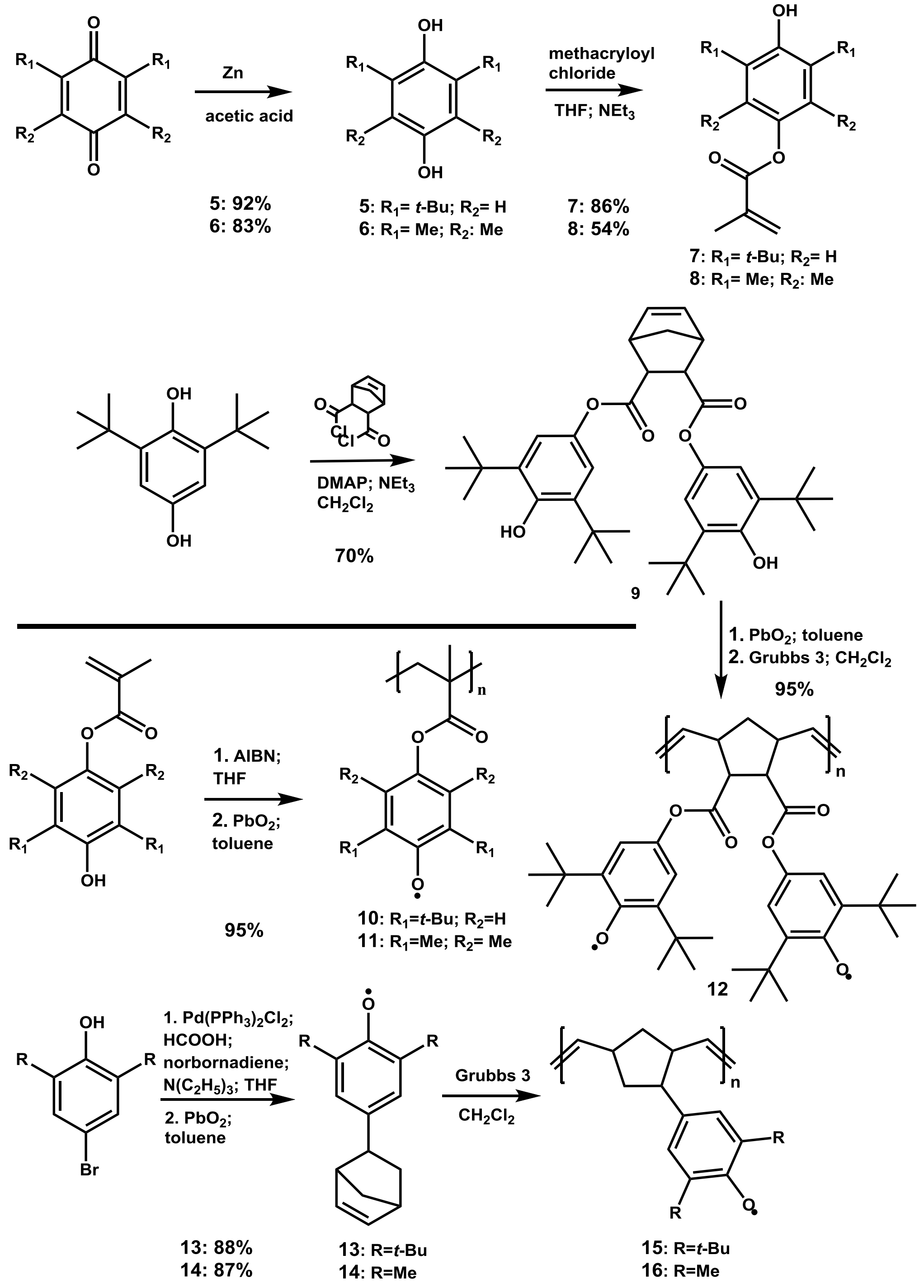


Figure 3-1. a) Cyclic voltammogramm of **4** (0.1 V/s; 0.1 M Bu_4NPF_6 in DMF). b) Charge/discharge curves (capacity *vs.* potential) of the 1st cycles of a half-cell of **4**.

Charge-capacities of up to 38 mAh/g could be measured, which corresponds to 70% of its theoretical capacity. Discharge-capacities were lower, with 27 mAh/g, which may be due to the non-optimal electrolyte, the unstabilized galvinolate-anion or self-discharge phenomena. To improve these systems further the electrolyte and in particular their pH values have to be optimized to accommodate both polymers, because both polymers function best under different pH-value conditions. Another possibility is, of course, the implementation of other, less pH-sensitive or higher capacity, electrode-materials.

3.2. Synthesis of phenoxyl-radical bearing polymers and their electrochemical behavior

The attempt to create redox-active polymers with higher theoretical capacities led to the smaller phenolic radicals, the phenoxyl-radicals. 2,6-Di-*tert*-butyl-4-methylphenol is often used as radical scavenger, because it can easily form radicals. These radicals, however, are not stable and dimerize as well as disproportionate shortly after their creation.[79] This can be explained by the distribution of the electron-spin density in the radical.[26] Because the *ortho*- and *para*-carbons possess a similar spin-density to the oxygen these positions are very reactive. In 2,6-di-*tert*-butyl-4-methylphenol the *ortho*-positions are blocked by the bulky *tert*-butyl groups, but the methyl-group in *para*-position is not sufficient enough to block reactions at this position.[30] Polymerizable groups could be introduced at the *para*-position, which would stabilize the final radical and also supply the polymeric backbone required for application in organic radical batteries. The substituents in *ortho*-positions can also be modified to decrease the molar mass of the monomer and, consequently, to increase the capacity, while keeping the radical-stability or to tune the redox-reactions potential. Synthetic strategies to obtain polymers with phenoxyl-radicals can be summarized to use either phenols or hydroquinones as starting materials. To obtain monomers for phenoxyl-polymers from phenols the polymerizable group is usually introduced by cross-coupling reactions. To this extent a bromine or iodine substitution in *para*-position is required. Some of these substances are commericially available, while in other cases the halogen-substituents are introduced *via* an electrophilic substitution using *N*-bromosuccinimide (NBS) or similar agents. Due to the substituents in *ortho*-position to the phenol the bromination-reactions only take place in 4-position. The introduction of a vinyl-group at this position and an ethynyl-group *via* Suzuki- and Sonogashira-reaction, respectively, was successful, but these compounds were not employed in ORBs, because the polymerizable groups do not stabilize the phenoxyl-radical completely. Polymerizable norbornene-substituents could be introduced *via* a reductive Heck-reaction to obtain monomers **13** and **14** (**Scheme 3-2**). An advantage of the norbornene-groups over other polymerizable groups, such as vinyl or methacrylate, is that compounds carrying this group can be polymerized even in their radical-form. The corresponding monomers were oxidized with PbO_2 and subsequently polymerized *via* ROMP using a 3rd generation Grubbs catalyst to yield the polymers **15** and **16**. The introduction of polymerizable moieties into hydroquinones is done through esterification of one of the hydroxides of the hydroquinone. Because hydroquinones **5** and **6** are sensitive to air and oxidize relatively quickly to the corresponding quinone, these reactions were performed swiftly after the reduction of the quinone to the hydroquinone. The esterifications to methacrylates were performed using methacryloyl chloride to obtain compounds **7** and **8** (**Scheme 3-2**). The acid chloride was added in excess to compounds where one hydroxyl-group was flanked by bulky substituents and the other was not. If the steric protection of one was not given the methacryloyl chloride was added in an equivalent amount. *Bis*-substituted norbornene **9** was also obtained *via* esterification of the norbornene-*bis*-acid chloride. The hydroquinone was added in slight excess to achieve complete functionalization of the compound. As with the mono-substituted norbornenes these were oxidized to the phenoxyl-radical before the ROMP-polymerization to yield polymer **12**. The obtained methacrylate-monomers were polymerized *via* free radical polymerization using AIBN and subsequently oxidized to the phenoxyl-radicals using PbO_2 to yield the polymers **10** and **11**. The obtained radicals were investigated for their redox-properties using cyclic voltammetry. The redox-potentials of the phenoxyl-radical polymers were not significantly influenced by their substitution-patterns. The compounds with *tert*-butyl- or methyl-substituents in ortho-position and methacryl and single-substituted norbornene as polymeric backbone showed redox-signals at –0.55 V (*vs*. Ag/AgCl). Only the di-substituted norbornene-phenoxyl compound featured a slightly lower redox-potential of –0.60 V (*vs*. Ag/AgCl) (**Figure 3-2**).



Scheme 3-2. Schematic representation of the synthesis of compounds **7**, **8**, **9**, **13** and **14** (top). Schematic representation of the synthesis of polymers **10** and **11** using free radical polymerization at 70 °C as well as synthesis of **5**, **6** by reductive Heck-reaction and polymers **12**, **15** and **16** by ring-opening metathesis polymerization (ROMP, bottom).

In continuation to the experiments performed with the galvinoxyl-polymers, charge-discharge experiments of the polymers were performed using a solution of sodium chloride and tetrabutylammonium hydroxide in water. The methacrylate-phenoxyl polymers exhibited 55% of their theoretical charging-capacity for the first charging-cycle, with steadily decreasing values for additional cycles.

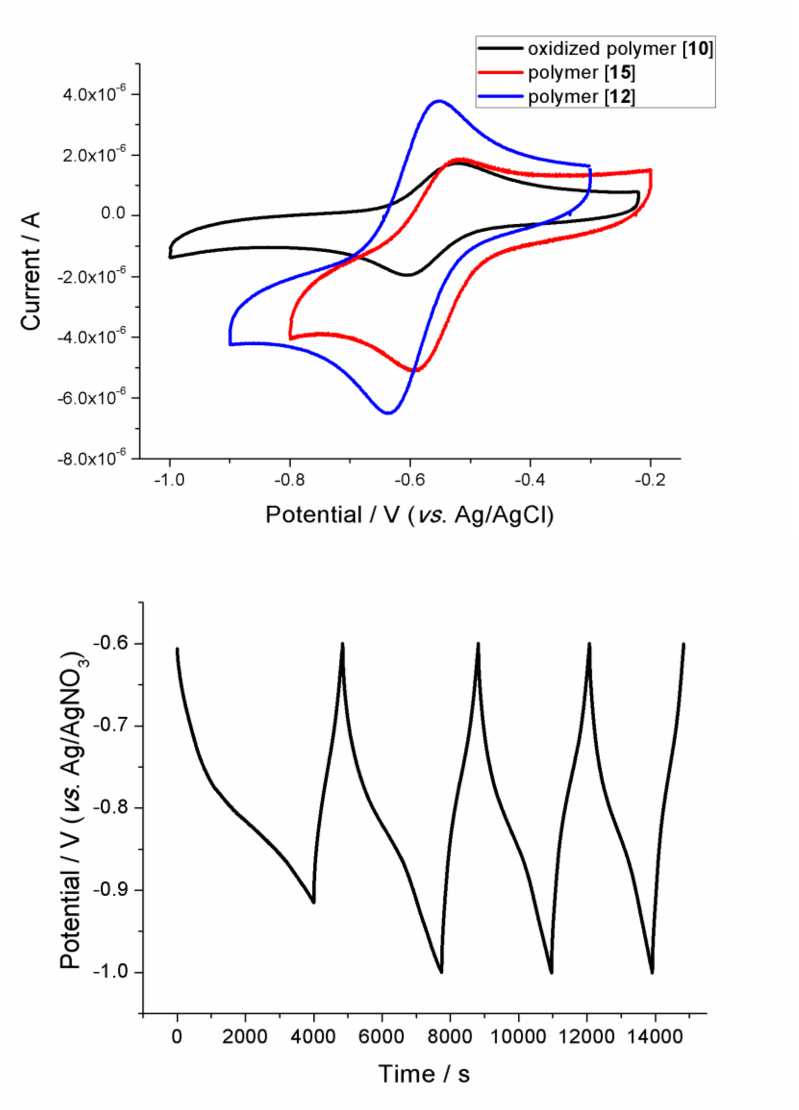


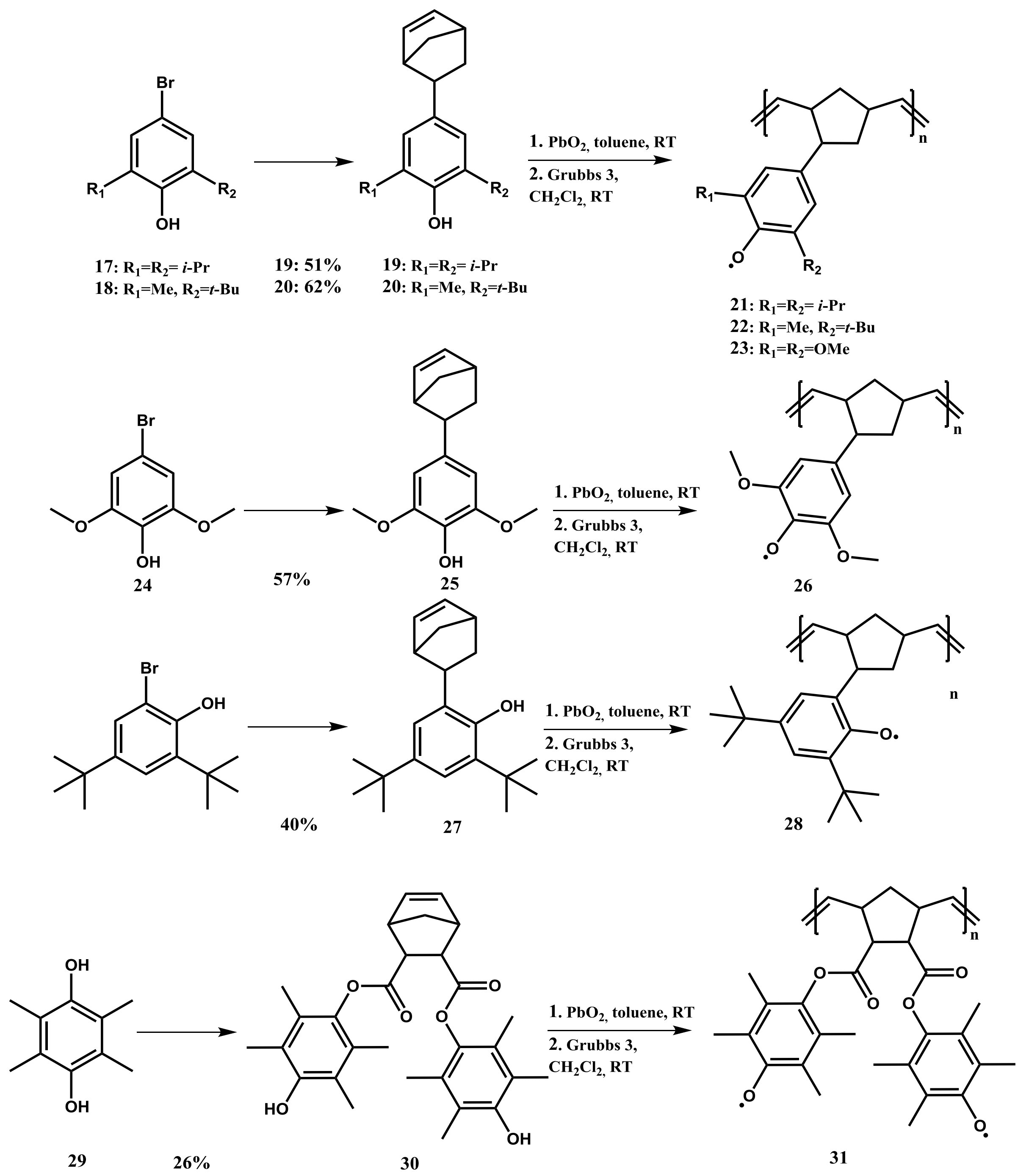
Figure 3-2. Cyclic voltammogramm of the oxidized polymers **10**, **15** and **12** (0.1 V/s; 0.1 M Bu_4NPF_6 in DMF) (top). Charge-discharge cycling of electrodes prepared from polymer **10** at 0.5 C using a solution of NaCl and tetrabutylammonium hydroxide in water (bottom).

Over 40 cycles the charging-capacities decrease from 51 to 18 mAh/g. The discharging-capacities amount to roughly 50% of the charging-capacities. The mono-substituted norbornene-polymers revealed a more stable behavior. The charging-capacities held steady at 72 mAh/g for several cycles, which corresponds to 80% of the polymers theoretical charge-capacity (**Figure 3-2**). This capacity decreases by 10% to 64 mAh/g after 50 cycles. The polymers discharge-capacities were measured to 40 mAh/g and remained largely unchanged for the measured 50 cycles.

3.3. Application of phenoxyl-radical polymers in lithium-batteries

To further test the capabilities of phenoxyl-radicals several other compounds were synthesized to investigate the influence of the different substituents and the ability to function in organic-lithium batteries. In case of the polymers **21**, **22**, **23** and **26** the substituents include combinations of methyl-, *iso*-propyl-, methoxy- and *tert*-butyl-groups in *ortho*-position to study the stability of the phenoxyl-radicals (**Scheme 3-3**). Polymer **28** with *tert*-butyl-groups in 2- and 4-position and the polymerizable group in *ortho*-position to the phenoxyl-radical center was also synthesized to study the stability of the polymerizable group. Starting from the corresponding phenolic compounds the phenoxyl-norbonene-polymers with 2,6-di-*iso*-propyl-, 2-*tert*-butyl-4-methyl-, 2,6-di-methoxy- and 4-6-di-*tert*-butyl-substituents were prepared. The phenolic compound was, if necessary brominated using NBS in acetonitrile to obtain the compounds **17** and **18**. For the bromination to the 2,6-dimethoxy-compound **24** a different method employing NBS, ethanol and sodium hydride in chloroform was employed. A *bis*-substituted norbornene **30** was also synthesized starting from duroquinone. This was reduced with Zn/NH_4Cl in acetic acid to give the hydroquinone **29**, which was then esterificated with *trans*-5-norbornene-2,3-dicarbonyl chloride. All monomers were oxidized with PbO_2 and subsequently polymerized *via* ROMP using a 3rd generation Grubbs catalyst with a monomer to catalyst ratio of 100 to 1. Phenoxyl-polymers **21**, **22**, **23**, **26** and **31** were obtained with molar masses (M_n) between 20,000 and 30,000 g/mol and conversions of 80% and above. Only polymer **28**, with the norbornene-group in *ortho*-position, gave lower yield (62%).

All polymers were investigated for their electrochemical properties using cyclic voltammetry. Depending on their substitution-patterns the polymers showed CV-signals between –0.55 and –0.67 V (*vs*. Ag/AgCl). All compounds were exposed to up 30 reduction-oxidation cycles and different scan-speeds with no degradation of the signal. As the most promising of the polymers and the one with the highest theoretical capacity and lowest redox-potential the *bis*-substituted phenoxyl-polymer **31** was used to build a lithium-organic coin-cell battery. A 1 M solution of $LiPF_6$ in propylene carbonate was used as electrolyte. The battery was charged and discharged at a constant rate of 1C, which corresponds to charging and discharging in one hour. ESR-measurements of the polymers revealed a radical-content of approximately 80%.



Scheme 3-3. Schematic representation of the synthesis of compounds **17** to **31**.

The cell showed a stable behavior for 100 cycles. The first cycle reached a charge-capacity of 67.1 mAh/g and a discharge-capacity of 64.9 mAh/g (**Figure 3-3**). The cells maximum charge-capacity is reached in the third cycle with 69.0 mAh/g and decreases afterwards slowly until after 100 cycles a charge-capacity of 57.4 mAh/g and a discharge-capacity of 54.0 mAh/g can be measured (**Figure 3-3**).

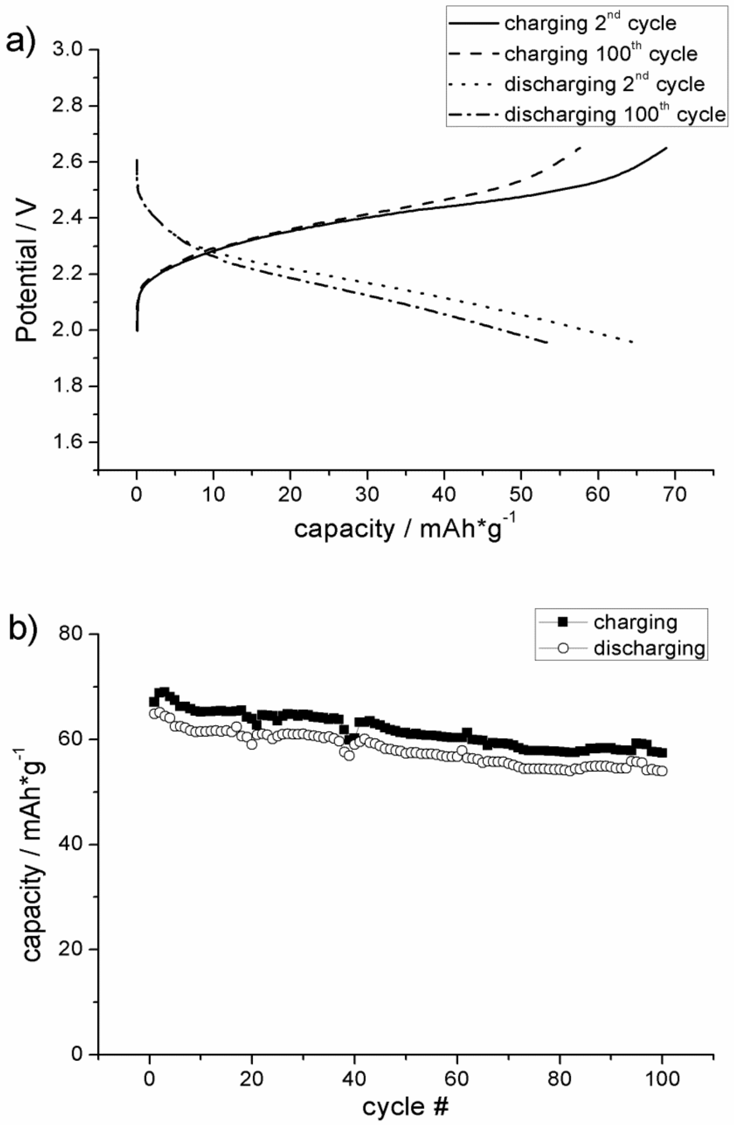


Figure 3-3. Charge-discharge cycles of polymer [**E**] at 1C in a lithium-organic coin-cell displayed as a) single cycles and b) as capacities for measured cycles. The inconsistencies in the b) are due to the change from day to night and temperature variations during the measurement.

When the cell is charged at a rate of 2C a maximum is reached in the second cycle with a charge-capacity of 67.1 mAh/g and a discharge-capacity of 61.9 mAh/g. The capacities decrease more rapidly than at 1C and after 94 cycles 45.6 mAh/g for the charge-capacity and 42.7 mAh/g for the discharge-capacity were determined. These results are promising and with further optimization of the electrolyte as well as electrode-morphology they can possibly be improved.

4 *n*-Type nitroxide-structures and quinone-derivatives as low-potential anode-materials

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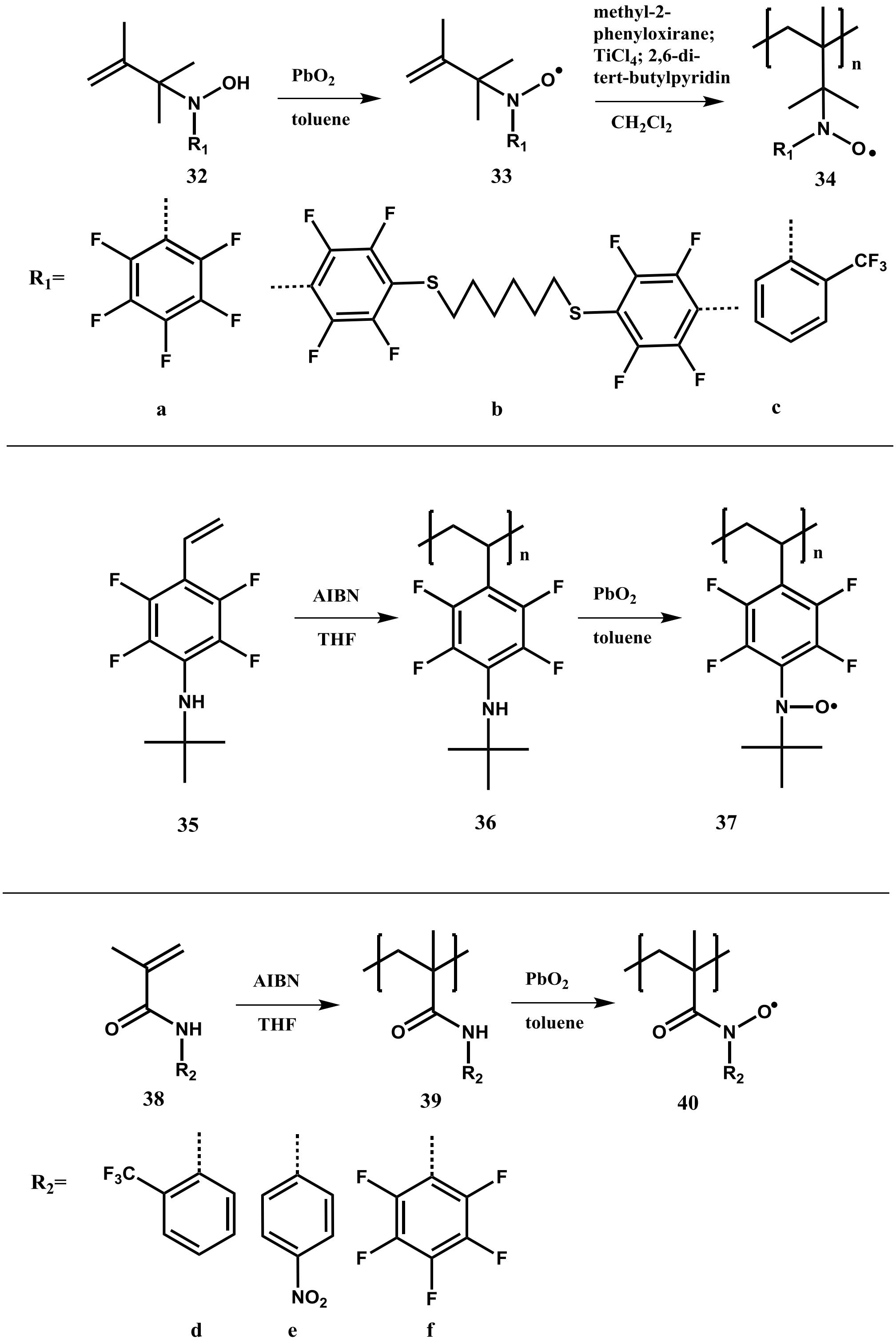
4.1. Synthesis of *n*-type nitroxide polymers and their electrochemical behavior

Nitroxide-radicals are probably the most well-known redox-active compounds. Their redox-behavior stems from the reversible reaction of the nitroxide-radical to either the oxammonium-cation or the aminoxyl-anion.[1, 2] The stabilities and the redox-potentials vary depending on the compounds structure – either embedded in a ring or in linear structures – and their substitution-patterns. Previous to the application in organic radical batteries, nitroxide-radicals were used for decades as mediators in a controlled radical polymerization, the so-called nitroxide mediated polymerization, as radical scavengers and ESR-labels.[17] With the first publication by Nakahara *et al.* in 2002 about ORBs the focus on nitroxide-research has shifted to this topic.[5] The first nitroxide porphyrexide, an inorganic nitroxide, was discovered more than 150 years ago by Piloty and Schwerin.[80] Today hundreds of stable nitroxide-radicals are known. The most prominent are the TEMPO- and the PROXYL-radicals. These radicals are the most common used in organic radical batteries. Other nitroxides with acyclic structures and bulky substituents in *ortho*- and *para*-positions to the radical, like *tert*-butyl and phenyl, are much less common, but give a much easier way to functionalize the structures and to adjust the redox-potentials.[2] Most nitroxides described in literature are only used as cathode-materials, because they can be reversibly oxidized to the oxammonium-cation, but the reduction to the aminoxyl-anion is not reversible.[1] However, there are a few examples of nitroxides which feature *n*-type behavior. These literature-examples are often functionalized acyclic nitroxides with trifluoromethyl-groups.[13] To supplement the research on anode-materials for organic radical batteries and on *n*-type nitroxide-structures several polymers carrying *n*-type nitroxides were synthesized (**Scheme**

4-1). The polymers are based on *iso*-butylene-, methacrylate- and styrene-units as polymeric backbones. To achieve *n*-type redox-abilities trifluoromethyl-, nitro- and perfluorated styrene-groups were introduced as substituents.

The *iso*-butylene-compound **34a** was synthesized starting from pentafluoroaniline. In the first reaction step pentafluoroaniline was treated with formic acid and hydrogen peroxide to yield the deep blue pentafluoro nitrosylbenzene. This compound was then functionalized with tetramethylethylene to form *N*-(2,3-dimethylbut-3-en-2-yl)-*N*-(pentafluorophenyl) hydroxylamine **32a**. Another *iso*-butylene monomer **32b** could be obtained by thio-"click" reaction of **32a** compound with 1,6-hexandithiol. The hexanedithiol was subsequently functionalized at the thiol-groups through the reaction with *para*-fluorine of the pentafluoro-compound. The *iso*-butylene monomer **32c** with a trifluoromethyl-substituent was synthesized by reaction of 2-trifluoromethyl aniline with formic acid and hydrogen peroxide and following a functionalization with tetramethylethylene. Compound **35** was synthesized by functionalization of pentafluorostyrene 4-position with *tert*-butylamine. Apart from *iso*-butylene and styrene-monmers, compounds **38d-f** containing methacrylamide as polymerizable group were also synthesized. Therefore 2-trifluoromethyl aniline, 4-nitro aniline and pentafluoroaniline were each functionalized with methacryloylchloride to obtain the corresponding methacrylamide-monomers. The polymerization of the monomers is the next step to obtain *n*-type nitroxide polymers. Because of the different polymerizable groups different polymerization techniques had to be employed. The polymerization of the *iso*-butylene compounds **32a-c** is only possible *via* cationic polymerization. 2-Methyl-2-phenyloxirane was used as initiator, titanium tetrachloride as co-initiator and 2,6-di-*tert*-butylpyridine as proton-trap for this reaction. To avoid reactions of the amine-units with the titanium tetrachloride the monomers were oxidized with PbO_2 beforehand to yield **33a-c**. Polymerization of the bis-functional monomer **33b** resulted in an insoluble polymer. The other isobutylene-polymers **34a** and **34c** were obtained with molar masses of approximately 10,000 g/mol (M_n). The styrene-monomer **35** was polymerized *via* free radical polymerization and a molar mass of 16,800 g/mol (M_n) was achieved.



Scheme 4-1. Schematic representation of the synthesis of compounds **32** to **40**.

The methacrylamide-monomers **38d-f** were also polymerized with AIBN *via* free radical polymerization techniques and molar masses between 10,000 and 20,000 g/mol (M_n) could be achieved. Because a free radical polymerization is not possible with radical-compounds, the styrene- **36** and methacrylamide-polymers **39d-f** had to be oxidized with PbO_2 after polymerization to yield polymers **37** and **40d-f**.

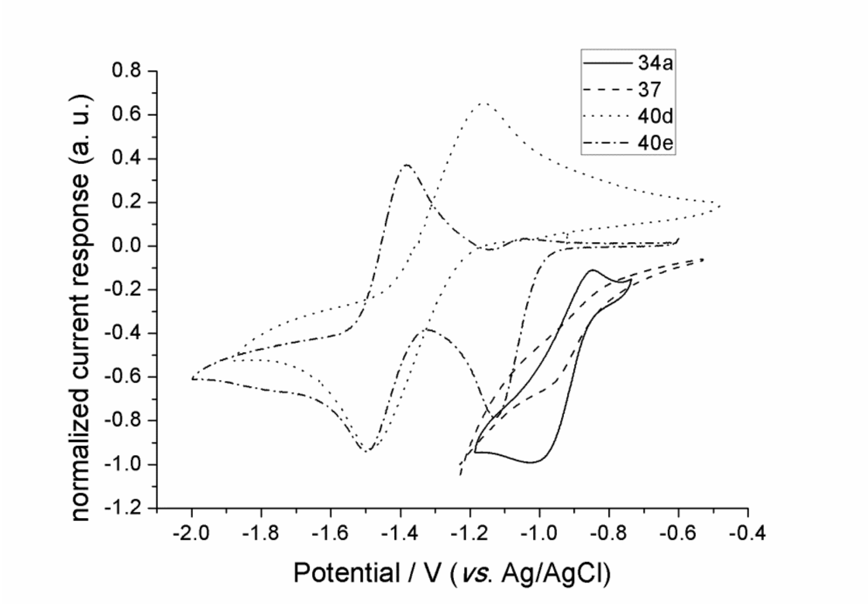


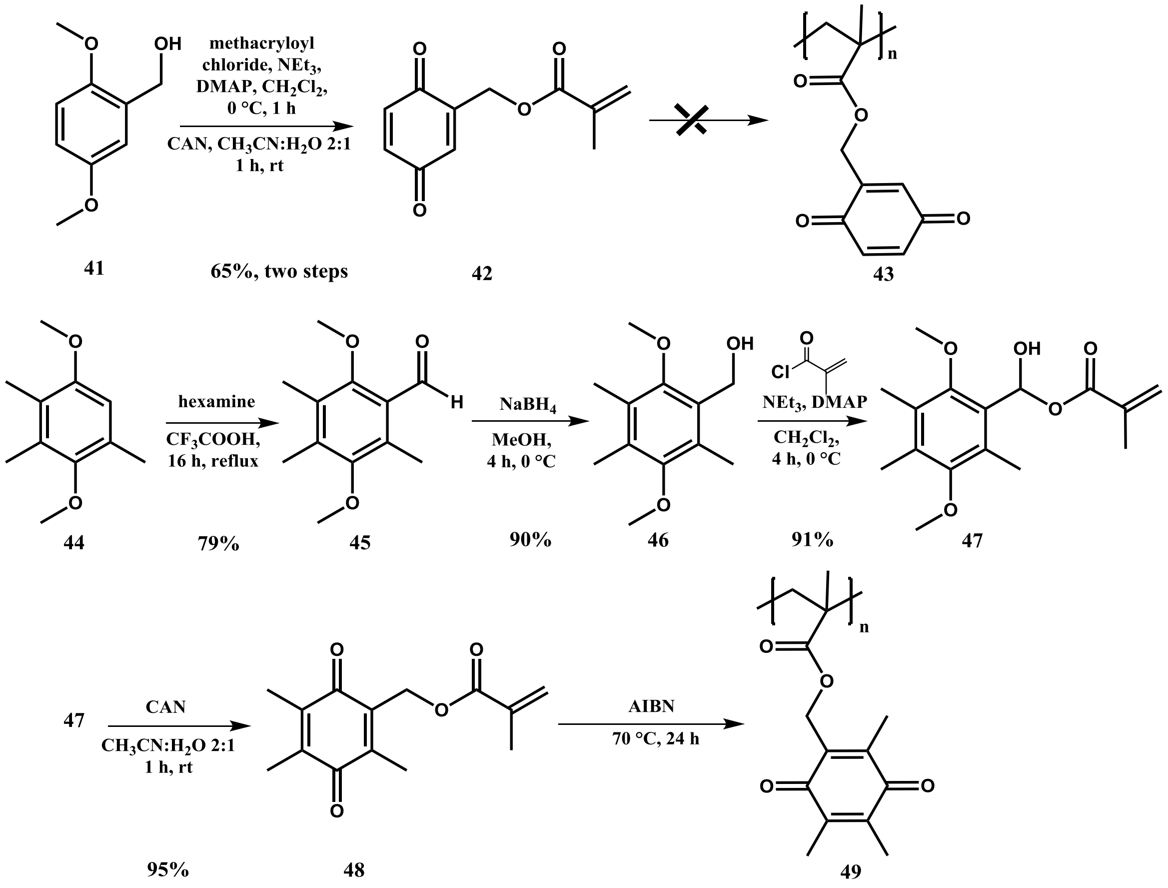
Figure 4-1. Cyclic voltammogramms of polymers [**34**], [**37**], [**40d**] and [**40e**] (0.1 V/s; 0.1 M Bu_4NPF_6 in DMF).

The obtained *n*-type nitroxide-polymers were subsequently characterized *via* ESR to determine the concentration of radicals in the polymer-chain. Radical-concentrations between 70 and 85% could be obtained. The *iso*-butylene polymers, which were oxidized before polymerization, revealed higher radical-concentrations than the other polymers. This stems from the coiled structures of the polymers, which make it more sterically hindered for the oxidizing agent to reach the target site. All polymers were then investigated with cyclic voltammetry to determine their redox-properties (**Figure 4-1**). The perfluorinated polymers **34a**, **34b**, **37** and **40f** all possess similar redox-potentials due to their similar structures. Their redox-potentials are situated between −1.28 and −1.34 V (*vs.* Fc/Fc^+). The other synthesized polymers show lower redox-potentials. The trifluoromethyl substituted polymers **34c** and **40d** show redox-potentials at −1.66 and −1.69 V (*vs.* Fc/Fc^+) respectively. The nitro-substituted polymer **40e** exhibits two distinct redox-potentials, because of the nitro-groups redox-activity. Its redox-potentials can be found at −1.45 and −1.78 V (*vs.* Fc/Fc^+).

These results point to a potentially promising future for these compounds, because the discerned redox-potentials are lower than the previously reported literature examples. Most other *n*-type nitroxides show their redox-potentials around –1.1 V (*vs.* Fc/Fc$^+$). With the help of these new nitroxides it would be possible to build batteries with higher potentials than possible with current *n*-type nitroxides, but this also brings problems due to the possibility that the electrolytes disintegrate during the electrochemical process.

4.2. Synthesis, polymerization and electrochemical behavior of quinone-derivatives

Quinoide compounds have been widely studied for their remarkable properties, simple synthesis and interesting electrochemical properties.[81] They are also widely used as radical scavengers, capacitor materials, redox resins, for their pharmacological properties or as dyes. Quinoides have also found recent attention in the field of organic electronics for their high charge-capacity, fast rechargeability and excellent cycle-stability.[82] They have been employed as high-density electrode-materials in organic, metal or air-batteries and even function in aqueous electrolytes.[82]



Scheme 4-2. Schematic representation of the synthesis of compounds **41** to **49**.

To supplement this interesting research-topic, polymers based on benzoquinones and functionalized anthraquinones as redox-active species were synthesized and electrochemically characterized.

Benzoquinones possess a reversible two-electron redox-behavior, whose redox-potential can be easily modified by functionalization with different substituents. Additionally the redox-behavior is also dependant on the electrochemical environment, consisting in batteries of electrolytes and conducting salts. The electrochemical reaction is highly influenced by the solvent. In organic solutions the reduction follows two separate one-electron reactions from the quinone to the semiquinone to the hydroquinone, respectively. In aqueous solutions, however, the reaction depends on the pH-value. While in acidic solutions the process follows the one electron reduction – hydrogen transfer mechanism, under basic conditions only one two-electron reaction can be found.[82] For the use as battery material in solid state organic batteries it is first required to obtain a polymer which is insoluble in the electrolyte.[1] Polymers containing quinone-units in the backbone are widely investigated, but as pendent groups they are less known.[81, 83] To obtain high molar mass polymers with quinone pendant-groups typical living polymerization procedures cannot be applied due to interactions between the quinone-moiety and the initiating or propagating species in the polymerization. Due to their radical-scavenging ability, radical polymerizations of quinone-monomers are also very difficult. A solution to this can be the introduction of protecting groups or a post-polymerization modification. Both possibilities lead to an incomplete functionalization of the polymer. To obtain a fully functionalized, high molar mass quinone-polymer the fully methyl-substituted quinone-monomer **48** was synthesized (**Scheme 4-2**). In this monomer the substituents at 2-, 3- and 5-positions on the benzoquinone suppress a potential radical-formation. To investigate the behavior of unsubstituted quinones the methacrylate-monomer **42** was synthesized in two steps starting from 2,5-dimethoxy benzylalcohol **41**. This compound was first substituted with methacryloylchloride and oxidized with cerium ammoniumnitrate. Unfortunately the polymerization using AIBN as initiator yielded no polymer. To obtain a fully methyl-functionalized quinone-polymer, which can be polymerized this way, a synthesis strategy starting from 2,3,5-trimethylhydroquinone was developed. In this synthesis route the phenolic groups were first protected as methoxy-groups to yield **44**, followed by the introduction of an aldehyde-group *via* a Duff-reaction to obtain **45**. The aldehyde was reduced to the alcohol-compound **46** with sodium borohydride and subsequentially functionalized using methacryloyl chloride to yield monomer **47**. The quinone-monomer **48** was obtained by the oxidation with CAN.

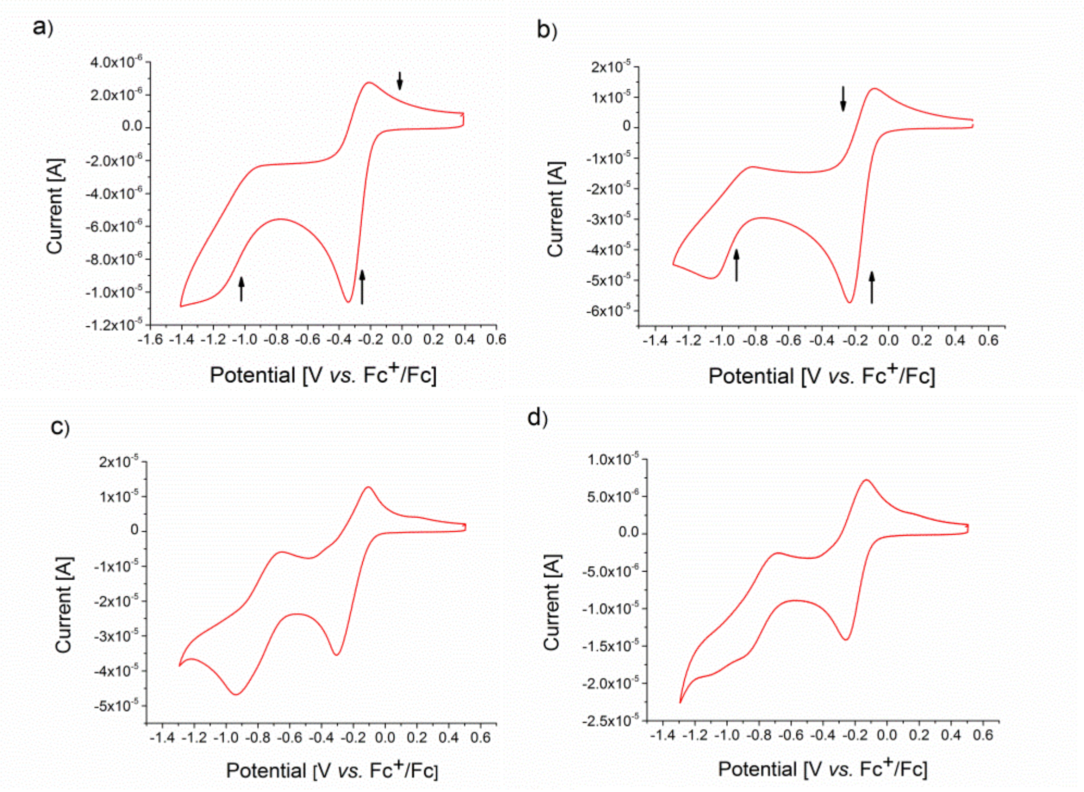


Figure 4-2. Cyclic voltammogramms of monomer **48** and polymer **49** at room temperature. a) Dropcast of **49** in propylene carbonate, 0.1 M $TBAClO_4$, scan rate 0.1 V/s; b) dropcast of **49** in acetonitrile, 0.1 M $TBAClO_4$, scan rate 0.1 V/s; c) 20 mM solution of **48** in dichloromethane, 0.1 M $TBAClO_4$, scan rate 0.1 V/s; d) 20 mM solution of **49** in dichloromethane, 0.1 M $TBAClO_4$, 0.1 V/s.

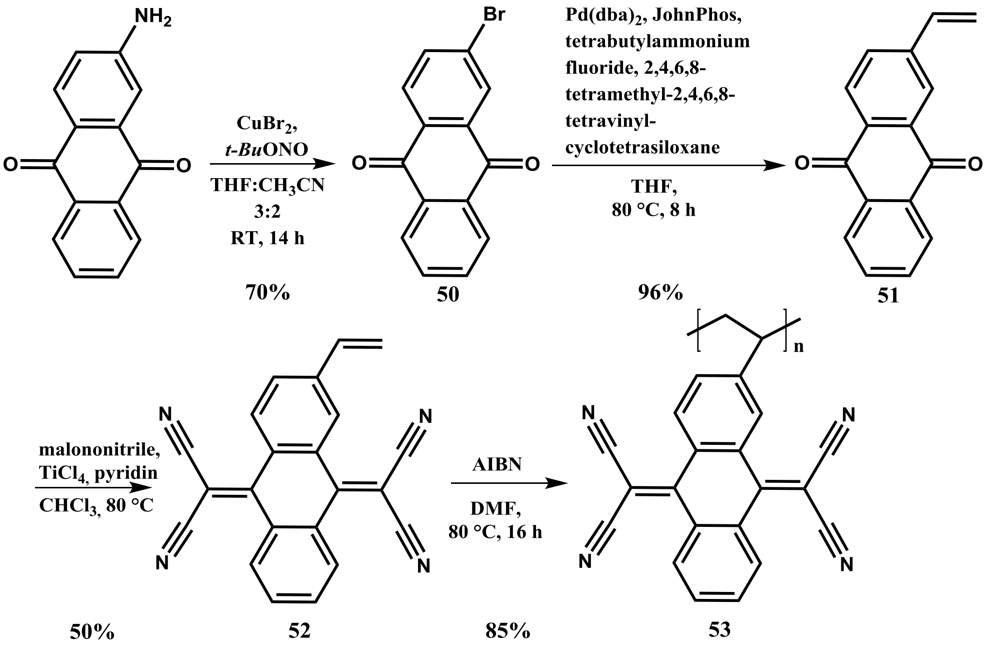
The polymerization-behavior of this compound using AIBN as initiator was investigated employing solvents with different polarities. Polar aprotic solvents such as DMF and DMAc gave the polymers with the highest molar mass and the highest conversion, while polar protic, unpolar and chlorinated solvents yielded lower conversions and molar masses. The best results were achieved using 1,4-dioxane as solvents. This polymerization to **49** gave a polymer with a molar mass of 17,400 g/mol (M_n), with a dispersity of 3.3 at 97% conversion. 5 mol% of initiator was used for this polymerization. Lower amounts decreased the yield and molar masses significantly, while higher amounts delivered almost the same results. To obtain insoluble polymers a copolymerization with a dimethacrylate with a triglyme-spacer was also performed.

The electrochemical behavior of the polymers was then investigated *via* cyclic voltammetry and rotating disc electrode experiments. Polymer **49** was dropcasted on a glassy carbon electrode and then measured in several different solvents under different pH-values. In propylene carbonate, the polymer revealed two redox-signals at –0.34 and –1.21 V (*vs*. Fc/Fc^+), while in acetonitrile they were observed at –0.23 and –1.05 V (*vs*. Fc/Fc^+) (**Figure 4-2**). The redox-signals decrease over the number of cycles and with the addition of lithium-salts they become completely irreversible. In dichloromethane the signals were found at –0.20 and –0.80 V (*vs*. Fc/Fc^+), respectively. The first reaction is quasi-reversible, while the second one is irreversible (**Figure 4-2**). The best results were obtained in 0.1 M aqueous $HClO_4$ as electrolyte. Two redox-signals could be found at around 0.51 V (*vs*. SHE). Rotating-disc electrode experiments revealed the lower-potential reduction-wave to be kinetically controlled, while the higher is diffusion controlled.

4.3. Functionalization of anthraquinone-compounds, their polymerization and electrochemical behavior

Apart from simple benzoquinones larger quinones like anthraquinone have also been intensively investigated regarding their electrochemical properties.[84] They have attracted interest due to their excellent stability and charge-discharge behavior as well as the possibility to use them as organic semiconductors.[85] Unlike other redox-active groups, with redox-reactions involving two electrons, the redox-reaction of anthraquinones does not occur at different potentials.[86] Starting from this advantage a functionalized anthraquinone-polymer was designed. Poly(2-vinyl-11,11,12,12-tetracyano-9,10-anthraquinonedimethane) employs TCAQ-units as redox-active groups and features one reversible two-electron-redox-reaction similar to anthraquinone. The monomer could be synthesized in three steps starting with 2-aminoanthraquinone. The amino-group was converted to a bromine-group in **50** using a modified Sandmeyer-reaction (**Scheme 4-3**), employing $CuBr_2$ and *tert*-butylnitrite. On this position a vinyl-group was introduced using a Hiyama cross-coupling reaction using

$Pd(dba)_2$ as palladium source and JohnPhos as ligand, to obtain **51**. The anthraquinon carbonyl-functionalities were then transformed to dicyanomethane-groups by a Knoevenagel-reaction with malonitrile, titanium tetrachloride and pyridine and TCAQ **52** could be acquired. Monomer **52** was subsequently polymerized *via* free radical polymerization using AIBN as initiator in DMF and polyTCAQ **53** could be obtained (**Scheme 4-3**) with a molar mass of 26,400 g/mol (M_n). The molar mass of the polymer could easily be adjusted by using different solvents.



Scheme 4-3. Schematic representation of the synthesis of anthraquinones **50** to **53**.

Due to the bad solubility of the monomer and polymer low concentrations had to be used for these polymerizations and the polymers polymerized from DMF were insoluble in propylene carbonate and, thus, suitable for the use as battery material. A cyclic voltammogramm of the monomer in propylene carbonate was recorded and it exhibits one two-electron redox-reaction at –0.64 V (*vs.* Fc/Fc^+). The reason for both redox-reactions showing one signal is because the structure of the radical anion is twisted and destabilized. The addition of the second electron leads to rearomatization, so the redox-potential of the first reduction is lowered and both occur at the same potential. The redox-chemistry of the polymer was investigated as part of a composite electrode on a graphite-sheet. The CV shows also one two-electron redox-reaction with a reduction at –0.83 V and the reoxidation at –0.47 V (*vs.* Fc/Fc^+) (**Figure 4-3**). The slight shift compared to the monomer can be appointed to the high viscosity of the propylene carbonate and the thickness of the electrode. Lithium coin-cells were fabricated using the polymer, employing a 0.1 M solution of lithium perchlorate as electrolyte. The battery can be reversibly charged and discharged for 500 cycles, with an average cell voltage of 3.05 V for charging and 2.25 V for discharging.

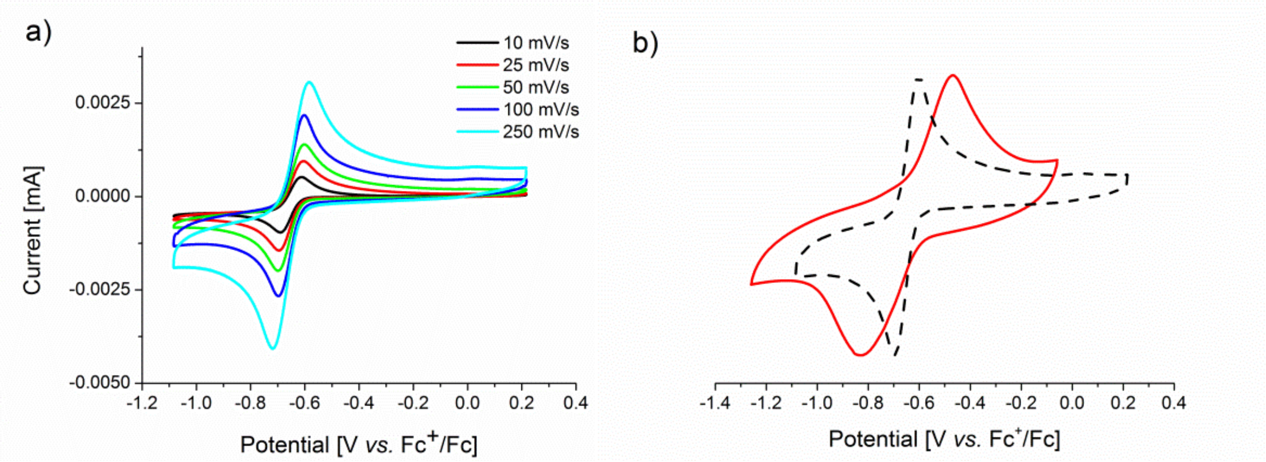


Figure 4-3. a) Cyclic voltammogramm of monomer **52** in propylene carbonate, 0.1 M lithium perchlorate at different scan rates (10, 25, 50, 100 and 250 mV/s, respectively). b) Normalized cyclic voltammogramms of the monomer **52** in solution (dashed black line) and a polymer-composite electrode (solid red line) (10/80/10 wt% **53**/VGCF/PVDF) in propylene carbonate, 0.1 M lithium perchlorate.

In the first cycle the material reaches 97% of its theoretical capacity, while after 500 cycles still 88% can be measured with a consistently high coulomb efficiency of 99% (**Figure 4-4**). This shows that the poly(TCAQ) is a promising organic electrode material with excellent capacity and stability.

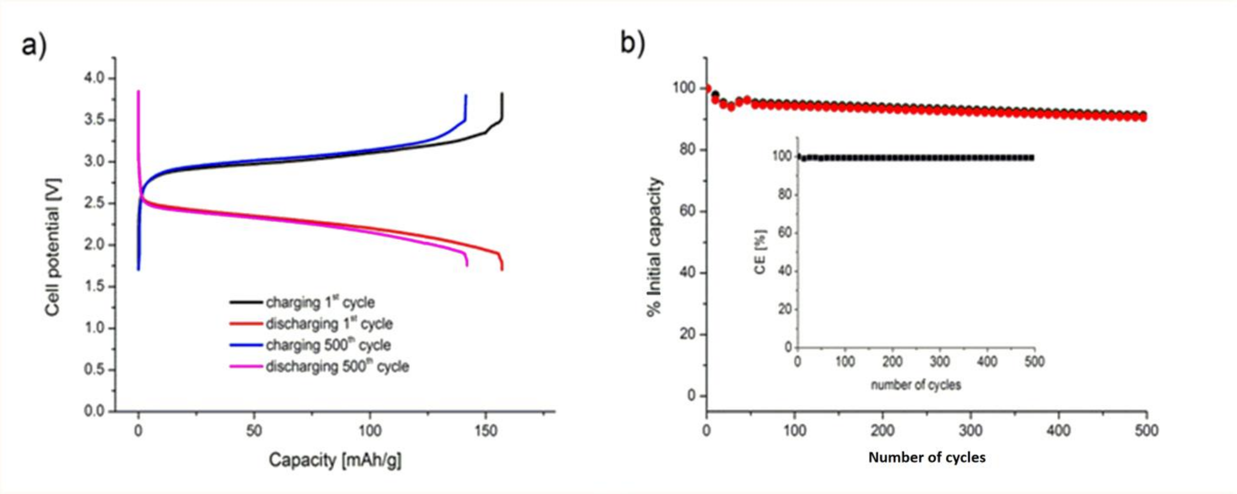


Figure 4-4. a) Charge/discharging curves (capacity *vs.* potential) of the Li-organic battery of the 1st and the 500th cycle. The anode is lithium metal, the cathode is a composite with poly(TCAQ) **31** as active material. b) Extended charge/discharge cycling of **31** in propylene carbonate, 0.1 M lithium perchlorate (500 cycles, 1 C). Coulombic efficiency (CE%) of 500 charge/discharge cycles (black squares).

5 Inkjet-printed nitroxide-cathodes for organic radical batteries

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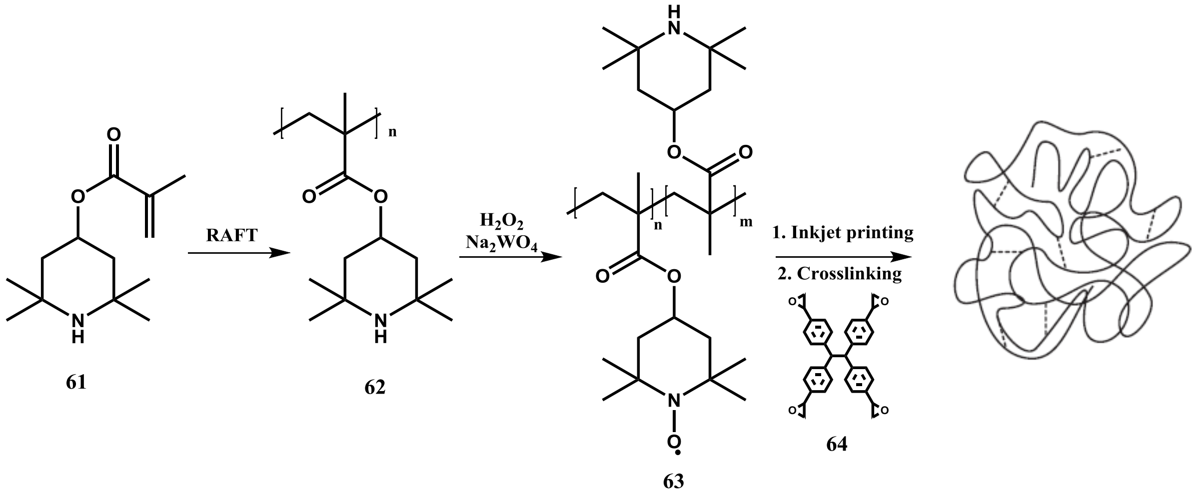
Till now many batteries used in hearing aids, medical patches and other consumer electronics are encased in rigid metal-casings.[1, 2, 18] Compared to organic electronics, like organic photovoltaic-powered electrochromic displays and LED lamps, the printing expertise for organic batteries is still lacking. Metal-based printed batteries using manganese dioxide and zinc for primary cells or lithium cobalt oxide and lithium for secondary cells exist,[8] but as with all metal-batteries they can cause unwanted environmental problems, in particular during disposal of such batteries. Organic radical batteries are much more environmental friendly,[1, 2] but the study of these is mostly focused on the development of new redox-active compounds, the modification of existing ones and the study of the electrolyte and the used conductive additives. For this simple processing-methods like doctor-blading or spin-coating are usually the preferred techniques. These processes often waste larger amounts of material and the resulting shape and size of the electrode is hard to control.[8]

With inkjet printing however almost no material is lost and the shape of the electrode is easy to control. The problem is though only easily soluble polymers can be used and only in solvents which are suitable for inkjet-printing. For organic radical batteries this constitutes a problem, because the polymers need to be insoluble in the batteries electrolyte. To overcome this problem defined polymers with low molar mass are required to be printed and, subsequently to be crosslinked to provide stable electrode-materials. Due to the presence of the TEMPO-radical and the conductive graphite-compound in the polymer-ink several crosslinking-techniques cannot be employed and a new approach had to be developed. For this approach PTMA was used as one of the most promising and stable radical polymers. The polymer is obtained by polymerization of the monomer 2,2,6,6-tetramethylpiperidin-4-yl methacrylate **61** and subsequent oxidation of **62** with *m*-chloroperbenzoic acid or hydrogen peroxide to **63** (**Scheme 5-1**). This oxidation-process is never complete and a co-polymer **63** is obtained. The remaining amino-moieties in the polymer can then be crosslinked with a multifunctional epoxide. Because the polymer shows a good thermal stability, thermal treatment of the printed structures can be utilized for the crosslinking process. To obtain the easily soluble polymer with the required rheological behavior (viscosity 0.4 to 20 mPas) the RAFT-polymerization was utilized. The used ink for inkjet printing also had to contain a conductive additive, but since the commonly used VGCF and graphite are too large for the nozzle (inner diameter 70 µm), carbon nanopowder (< 50 nm) was used. As solvent, DMF was found to be the most suitable solution. To this mixture 10% NMP was added to circumvent the coffee-ring-effect. The crosslinking-agent tetraphenylolethane glycidyl ether **64** is also part of this ink (**Scheme 5-1**). To prevent the formation of brittle films, which can peel off in the electrolyte, ethylene carbonate as plasticizer was added resulting in homogenous and stable films.



Scheme 5-1. Schematic representation of the synthesis of radical polymer poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) **62** (PTMA) by RAFT polymerization, oxidation to **63**, and subsequent thermal crosslinking with a multifunctional epoxide **64**.

The inkjet-printed films were then used as half-cells and repeatedly charged and discharged. The films without crosslinking showed no more activity after two cycles, but those with crosslinker kept 75% of their initial capacity after 150 cycles (**Figure 5-1**). The decrease can be attributed to the slow washing out of the active polymer from the composite. Therefore epoxidized carbon was prepared by reaction of carbon nanopowder with *m*-chloroperbenzoic acid. Through this the carbon itself acts as crosslinker and binds the active polymer. With this configuration the initial capacity of a test-cell was retained even after 150 cycles. Such an electrode was also used in a beaker-type battery employing zinc as anode-material and $ZnBF_4$ in propylene carbonate as electrolyte. The cell exhibits an average voltage of 1.25 V and a capacity of 20.5 µAh, which corresponds to a capacity of 50 mAh/g. This shows the possibility to use this technique to manufacture patterned, flexible organic batteries for use in sensors, smart packaging or DNA chips.

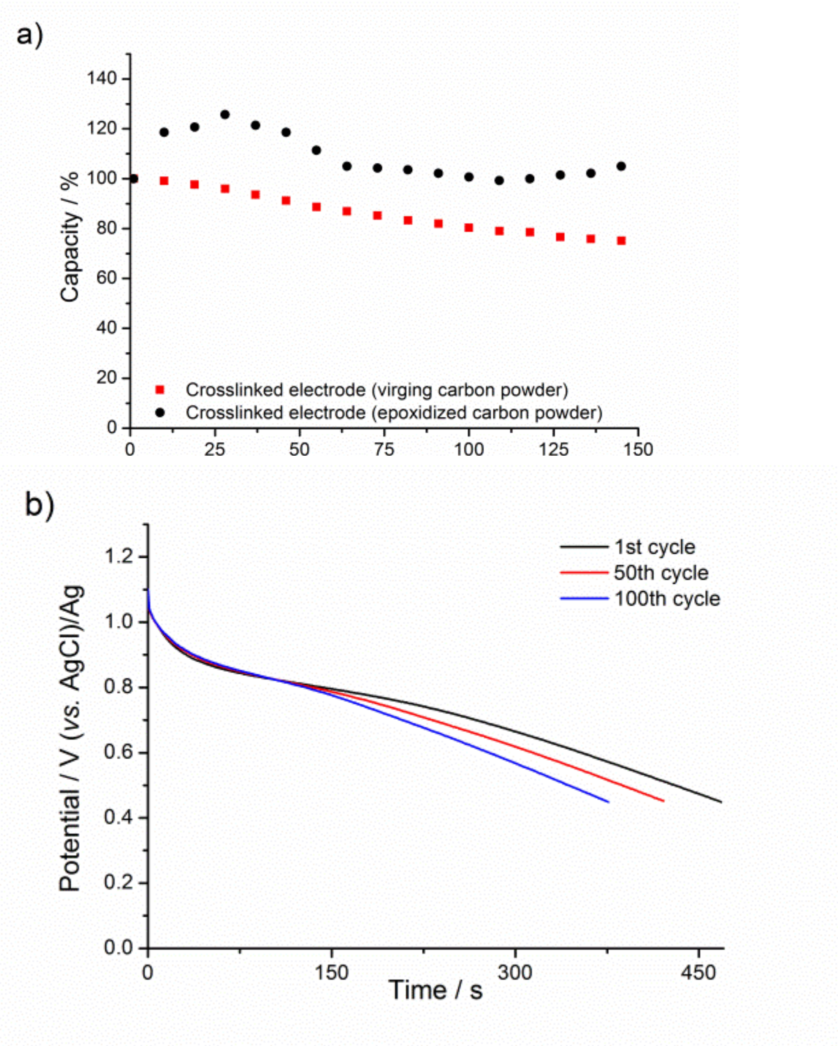


Figure 5-1. a) Cycling stability of inkjet printed electrodes at 1.5 A/m^2 over 150 cycles. b) Discharging curves of inkjet printed electrodes with non epoxidized carbon nanopowders at 1.5 A/m^2 using a solution of tetrabutylammonium hexafluorophosphate in propylene carbonate as electrolyte.

Summary

The development and synthesis of new polymers for organic batteries is a long and difficult process rife with challenges. However, the reward for this are suitable materials for the next generation of secondary batteries. The investigations within the scope of this thesis are focused on the discovery of new redox-active polymers suitable as active materials in batteries. These organic battery materials can compete with inorganic materials in terms of theoretical capacity, power and energy density. The most beneficial features of these compounds like light weight, flexibility, printability and environmental friendliness make them promising candidates for secondary organic batteries. With the vast repertoire of known redox-active species the transfer of those into a polymeric structure and their subsequent electrochemical testing can provide access to a wide variety of different electrode materials (**Figure S-1**). One category of redox-active materials that can be applied to organic batteries is known as antioxidants or radical scavengers. Some of the most well-known of those are based on galvinoxyl or phenoxyl as redox-active compound.

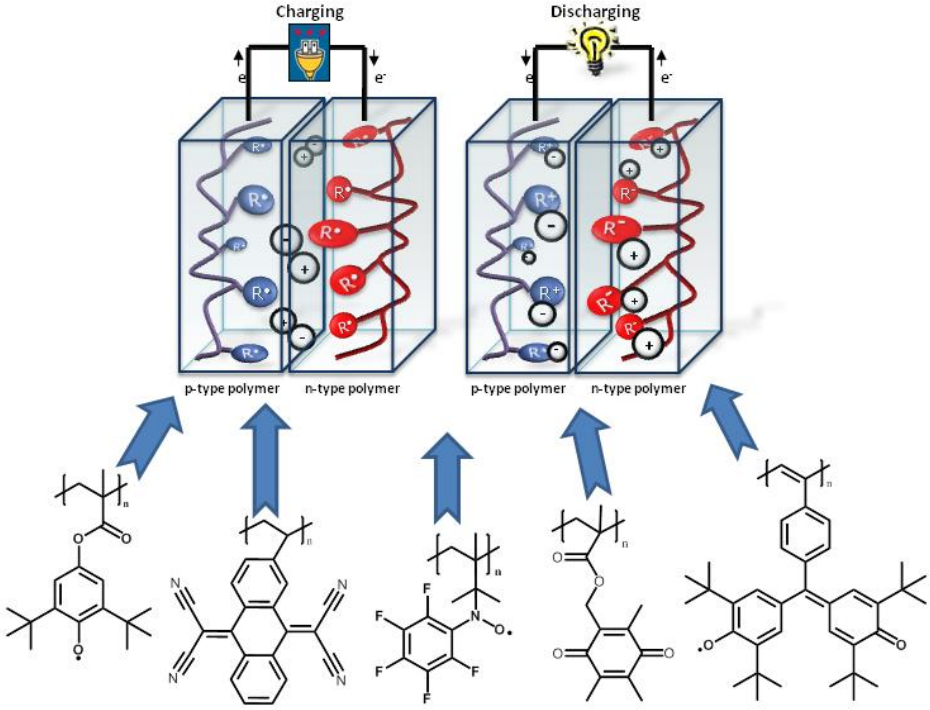


Figure S-1. Representation of the polymer classes used as materials for organic batteries.

Galvinoxyl containing polymers were one of the first anode-materials employed in organic radical batteries. The commonly used polymer is based upon a styrene-backbone. Within this context, galvinoxyls were introduced into another polymeric backbone, the polyacetylene. An all-organic battery with polymer **4** and PTMA was fabricated and showed a good performance in an aqueous electrolyte. To increase the theoretical capacity compared to the high molar mass galvinoxyls phenoxyl-radicals were incorporated into polymeric architectures. Following this concept several polymers could be obtained. The employed substituents varied between methyl-, *tert*-butyl-, *iso*-propyl-, methoxy-groups and combinations of those. The polymerizable group was based on methacrylate or norbornene. The norbornene based compounds **13**, **14**, **21-23**, **26** and **28** could be oxidized to the active radicals prior to polymerization, while the methacrylates **10** and **11** were polymerized first with subsequent oxidation of the polymers. Other polymerizable groups like vinyl or ethynyl could not stabilize the radical and, consequently, could not be used for battery applications.

The phenoxyl radical compounds feature a redox-potential around –0.6 V (*vs*. Ag/AgCl). Their charge-discharge behavior was investigated in water as electrolyte. The poly(norbornene)s showed promising properties with ca. 80% initial capacity, which only decreased to ca. 70% after 50 cycles. This displays that phenoxyl-compounds can be applied similarly to the bulkier galvinoxyl compounds. To further test the capabilities of phenoxyl polymers a *bis*-functionalized polymer **31** was used to fabricate a coin-cell with lithium as counter-electrode. The fabricated battery was based on $LiPF_6$ in propylene carbonate as electrolyte and was measured for 100 cycles. The battery featured a maximum charge capacity of 69.0 mAh/g, which decreased slowly to 57.4 mAh/g after 100 cycles. The discharge-capacity started at 64.9 mAh/g and decreased to 54.0 mAh/g after 100 cycles. These results are promising, but must be further improved by tailoring the electrolyte and the morphology of the electrodes to the active materials requirements.

Another class of potential anode-materials are *n*-type nitroxides. Several polymers bearing trifluoromethyl-, nitro- and fluorine-substituents were synthesized. The polymers **34**, **36**, **37**, **39** and **40** employed styrene-, iso-butylene- and methacrylamide-units as polymeric backbones. In addition to these polymers, quinone-polymers were also synthesized for the use as anode-active materials. The problem with those compounds is their radical-scavenging activity. Radical initiators can react with the quinone, stopping the reaction. A benzoquinone-methacrylate monomer was synthesized to test this and, as expected, the polymerization was unsuccessful. To overcome this problem, the monomer was completely substituted with methyl-groups. This benzoquinone-monomer was then polymerized to **49** *via* a free radical polymerization process with good results. Cyclic voltammetry measurements of the polymer and the monomer were conducted and, depending on the electrolyte and the pH-value, redox-potentials with one or two redox-waves between –0.15 and –0.79 V (vs. Fc/Fc^+) could be observed.

As another quinone-like derivative a tetracyano-substituted anthraquinone (TCAQ) was synthesized. 2-Vinylanthraquinone was functionalized *via* a Knoevenagel-reaction to obtain TCAQ, which was subsequently polymerized *via* free radical polymerization. The polymer **53** was evaluated in a lithium coin-cell. The battery reached 97% of the polymers theoretical capacity during the first cycle and still offered 88% after 500 cycles.

The development of new active materials is not the only goal of this thesis. Additionally the application of these materials in organic batteries is aimed for. Printing-techniques allow the fabrication of thin polymer films. This concept was applied to fabricate organic batteries. A mixture of active polymer **63** (PTMA) and carbon nanopowder was inkjet-printed. The incomplete oxidation of the radical-precursor and the so remaining amino-groups were used for a thermal crosslinking-procedure with an epoxide-compound. The crosslinked films exhibited a good electrochemical behavior even after 150 charging-discharging cycles.

To conclude, it could be shown that polymers employing redox-active moieties like galvinoxyl, phenoxyl or nitroxide and others represent promising active materials for the use in organic batteries. The presented results reveal a part of the relationship between electrochemical properties and the compounds structure and can be seen as a step towards tailor-made electrode-materials and environmental friendly batteries. To use these batteries in applications, e.g., in consumer electronics, medical gadgets or in printed electronics the capacities have to be further developed. One large problem is still the expensive price and the sometimes difficult synthesis. Until these problems are solved an industrial application is still far in the future. Problems like these, however, cannot stop the development of the potentially next big step in battery-technology and should be rather seen as challenges than as hindrances.

Zusammenfassung

Die Entwicklung und Synthese neuer Polymere für organische Batterien ist ein langer und aufwendiger Prozess mit vielen Herausforderungen, aber er ist nötig um geeignete Materialien für die nächste Generation von Sekundärbatterien zu erhalten. Die Untersuchungen innerhalb dieser Arbeit beziehen sich auf die Entdeckung neuer redoxaktiver Polymere als Aktivmaterialien in Batterien. Diese Batteriematerialien können mit anorganischen Materialien im Bezug auf theoretische Kapazität, Strom- und Energiedichte konkurrieren. Der größte Vorteil solcher organischer Verbindungen ist jedoch ihr geringes Gewicht, Flexibilität, Druckbarkeit und Umweltfreundlichkeit. Durch eine große Auswahl an redoxaktiven Spezies führt der Transfer dieser in Polymerstrukturen zu einer großen Vielfalt an Elektroden-Materialien (**Figure S-2**). Eine Kategorie der redoxaktiven Materialien, die in organischen Batterien verwendet werden kann, sind Antioxidantien und Radikalfänger. Die bekanntesten davon basieren auf Galvinoxyl- oder Phenoxyl-Strukturen.

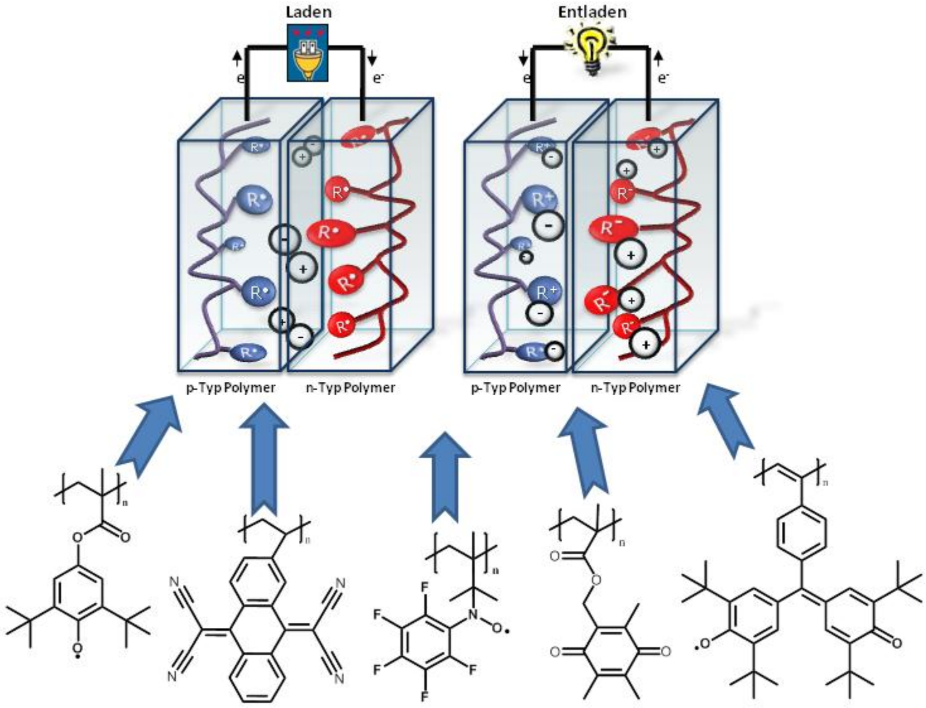


Figure S-2. Representation der Polymerklassen, die als Materialien in organischen Batterien verwendet wurden.

Galvinoxyle sind für ihre erstaunliche Stabilität gegenüber Feuchtigkeit und Oxidationsmitteln sowie für ihre stabile Redoxreaktion bekannt. Galvinoxyl-haltige Polymere waren unter den ersten Anoden-Materialien, die in organischen Radikalbatterien verwendet wurden. Um die Bandbreite dieser Polymere zu erweitern, wurden Galvinoxyle mit Poly(acetylen) als Polymer **4** synthetisiert. Eine komplett organische Batterie dieser Poly(galvinoxyle) und PTMA konnte hergestellt werden und zeigte gute Leistungsdaten im wässrigen Elektrolyt. Um höhere theoretische Kapazitäten, verglichen mit Galvinoxyl, zu erreichen, wurden Phenoxyl-Radikale in verschiedene Polymerarchitekturen eingebaut. Diese besitzen Substituenten wie Methyl, *tert*-Butyl, *iso*-Propyl, Methoxy oder Kombinationen dieser und als polymerisierbare Gruppe Methacrylat- (**10** und **11**) oder Norbornen-Einheiten (**13**, **14**, **21-23**, **26** und **28**). Andere polymerisierbare Gruppen wie Vinyl und Ethinyl konnten das Radikal nicht stabilisieren und deswegen nicht in Batterien getestet werden. Die Phenoxyl-Radikal-Polymere besitzen Redoxpotentiale um –0.6 V (*vs*. Ag/AgCl). Ihr Lade/Entlade-Verhalten wurde in einem wässrigen Elektrolyten mit Natriumchlorid und Tetrabutylammoniumhydroxid getestet. Hierbei zeigten die Poly(norbornene) bessere Resultate, wobei anfänglich ca. 80% der theoretischen Kapazität erreicht wurden. Diese sank nach 50 Zyklen auf ca. 70% sank. Dies zeigt, dass Phenoxyle in ähnlicher Weise wie die schwereren Galvinoxyle verwendet werden können. Um die Fähigkeiten der Polymere weiter zu testen wurde eine Knopfzelle mit einem *bis*-funktionalisiertem Phenoxyl-Polymer **31** und Lithium als Gegenelektrode erstellt. Die Batterie besitzt eine maximale Ladekapazität von 69.0 mAh/g, die langsam auf 57.4 mAh/g nach 100 Zyklen abfällt. Im gleichen Zeitraum fällt die Entladekapazität von 64.9 mAh/g auf 54.0 mAh/g. Diese Resultate sind vielversprechend, allerdings müssen dennoch verbessert werden, durch Anpassung von Elektrolyt und Elektroden-Morphologie an die Bedürfnisse des Aktivmaterials.

Eine weitere Klasse von Anodenmaterialien sind *n*-Typ Nitroxide. Mehrere Polymere mit Trifuormethyl-, Nitro- und Fluor-Substituenten wurden synthetisiert. Diese Polymere **34**, **36**, **37**, **39** und **40** nutzen Poly(styrene), Poly(*iso*-butylene) und Poly(methacrylamide) in ihrem Polymer-Rückgrat. Andere *n*-Typ Nitroxide in der Literatur besitzen Redox-Potentiale um –1.1 V (*vs.* Fc/Fc^+), jedoch die hier synthetisierten Polymere haben Redox-Potentiale zwischen –1.3 und –1.8 V (*vs.* Fc/Fc^+). Zusätzlich zu diesen Materialien wurden auch Chinon-basierte Polymere als Anoden-Materialien synthetisiert. Das Problem mit diesen ist jedoch ihre Fähigkeit als Radikalfänger. So kann es dazu kommen, dass der Initiator vollständig mit dem Quinon reagiert. Zum Test wurde eine Polymerisation mit einem Benzochinon-Methacrylat durchgeführt, welche kein Polymer ergab. Um Polymere zu erhalten wurde ein komplett Methyl-substituiertes Benzochinon hergestellt und dann mittels freier radikalischer Polymerisation in guten Ausbeuten zu **49** polymerisiert. Cyclovoltammetrie-Messungen des Polymers zeigten eine Abhängigkeit des Redox-Potentials vom Elektrolyt und dem pH-Wert. Abhängig von den Bedingungen besitzt der Polymer ein oder zwei Redox-Wellen zwischen –0.15 und –0.79 V (*vs.* Fc/Fc^+). Als weiteres Chinon-Derivat wurde **52** (TCAQ) hergestellt. Dazu wurde 2-Vinylanthraquinon mittels einer Knövenagel-Reaktion funktionalisiert, welches dann anschließend mittels freier radikalischer Polymerisation zu **53** polymerisiert wurde. Dieses Polymer zeigte eine zwei-Elektronen Redox-Welle bei –0.64 (*vs.* Fc/Fc^+) und wurde weiterhin in einer Lithium-Knopfzelle vermessen. Die Batterie zeigt 97% der theoretischen Kapazität des Polymers während des ersten Zyklus. Nach 500 Lade-Entlade Zyklen sind immer noch 88% der theoretischen Kapazität vorhanden. Die Entwicklung neuer Aktivmaterialien war nicht das einzige Ziel dieser Arbeit, sondern auch diese in organischen Batterien anzuwenden. Der Einsatz von Druck-Techniken erlaubt es dünne Polymer-Filme herzustellen. Dieses Konzept wurde auf ORBs angewandt und eine Kombination aus **63** (PTMA) und Kohlenstoff-Nanopulver wurde mittels Tintenstrahldruck verarbeitet. Durch die unvollständige Oxidation des Radikal-Vorgängers und den so noch vorhandenen Amino-Gruppen ist es möglich, das Polymer thermisch mittels eines Epoxids zu vernetzen. Die vernetzten Filme zeigten gutes elektrochemisches Verhalten auch nach 150 Lade-Entlade Zyklen.

Es ließ sich zeigen, dass Polymere mit redox-aktiven Einheiten wie Galvinoxyl, Phenoxyl oder Nitroxid und andere, vielversprechende Aktivmaterialien für organische Batterien darstellen. Die präsentierten Resultate helfen beim Ausbau des Verständnisses der Beziehung zwischen elektrochemischen Eigenschaften und der Struktur eines Moleküls. Dies kann als Schritt in Richtung maßgefertigter Elektrodenmaterialien und umweltfreundlicher Batterien gesehen werden.

Für Anwendungen sind jedoch noch weitere Forschungsanstrengungen nötig und Probleme wie der hohe Preis und schwierige Synthesen polymerer Aktivmaterialien dürfen uns nicht von dem nächsten großen Durchbruch der Batterie-Forschung abbringen.

References

1 T. Janoschka, M. D. Hager, U. S. Schubert, *Adv. Mater.* **2012**, *24*, 6397–6409.

2 K. Oyaizu, H. Nishide, *Adv. Mater.* **2009**, *21*, 2339–2344.

3 S. Muench, A. Wild, C. Friebe, B. Häupler, T. Janoschka, U. S. Schubert, *Chem. Rev.* **2016**, *116*, 9438–9484.

4 J. Winsberg, T. Hagemann, T. Janoschka, M. D. Hager, U. S. Schubert, *Angew. Chem. Int. Ed.* **2017**, *129*, 702–729.

5 K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, J. Iriyama, M. Suguro, E. Hasegawa, *Chem. Phys. Lett.* **2002**, *359*, 351–354.

6 A. Studer, T. Schulte, *Chem. Rec.* **2005**, *5*, 27–35.

7 Y. Wu, L. Bi, W. Bi, Z. Li, M. Zhao, C. Wang, J. Ju, S. Peng, *Bioorg. Med. Chem.* **2006**, *14*, 5711–5720.

8 T. Janoschka, A. Teichler, B. Häupler, T. Jähnert, M. D. Hager, U.S. Schubert, *Adv. Energy Mater.* **2013**, *3*, 1025–1028.

9 R. B. Grubbs, *Polym. Rev.* **2011**, *51*, 104–137.

10 K. Koshika, N. Sano, K. Oyaizu, H. Nishide, *Chem. Commun*. **2009**, *7*, 836–838.

11 S. Iwasa, M. Suguro, N. Natori, K. Nakahara, J. Iriyama, M. Satoh, H. Nishide, *Electrochim. Acta* **2004**, *50*, 827–831.

12 K. Oyaizu, T. Suga, K. Yoshimura, H. Nishide, *Macromolecules* **2008**, *41*, 6646–6652.

13 H. Nishide, K. Koshika, K. Oyaizu, *Pure Appl. Chem.* **2009**, *81*, 1961–1970.

14 K. Koshika, N. Chikushi, N. Sano, K.Oyaizu, H. Nishide, *Green Chem.* **2010**, *12*, 1573–1575.

15 T. Suga, H. Ohshiro, S. Sugita, K. Oyaizu, H. Nishide, *Adv. Mater.* **2009**, *21*, 1627–1630.

16 M. Suguro, A. Mori, S. Iwasa, K. Nakahara, K. Nakano, *Macromol. Chem Phys.* **2009**, *210*, 1402–1407.

17 T. Jähnert, T. Janoschka, M. D. Hager, U. S. Schubert, *Eur. Polym. J.* **2014**, *61*, 105–112.

18 Y. Liang, Z. Tao, J. Chen, *Adv. Energy Mater*. **2012**, *2*, 742–769.

19 T. Suga, S. Sugita, H. Ohshiro, K. Oyaizu, H. Nishide, *Adv. Mater.* **2011**, *23*, 751–754.

20 Y. Yonekuta, K. Susuki, K. Oyaizu, K. Honda, *J. Am. Soc. Chem.* **2007**, *129*, 14128–14129.

21 T. Jähnert, B. Häupler, T. Janoschka, M. D. Hager, U. S. Schubert, *Macromol. Chem. Phys.* **2013**, *214*, 2616–2623.

22 T. Kaneko, H. Abe, T. Namikoshi, E. Marwanta, M. Teraguchi, T. Aoki, *Synth. Met.* **2009**, *159*, 864–867.

23 T. Jähnert, B. Häupler, T. Janoschka, M. D. Hager, U. S. Schubert, *Macromol. Rapid Commun.* **2014**, *35*, 882–887.

24 M. Miyasaka, T. Yamazaki, E. Tsuchida, H. Nishide, *Polyhedron* **2001**, *20*, 1157–1162.

25 H. Nishide, M. Miyasaka, E. Tsuchida, *Angew. Chem. Int. Ed.* **1998**, *37*, 2400–2402.

26 R. G. Hicks, *Org. Biomol. Chem.* **2007**, *5*, 1321–1338.

27 L. Lu, S. Zhu, H. Zhang, S. Zhang, *Comput. Theor. Chem.* **2013**, *1019*, 39–47.

28 A. Tai, T. Sawano, F. Yazama and H. Ito, *Biochim. Biophys. Acta* **2011**, *1810*, 170–177.

29 X.-J. Qi, L. Liu, Y. Fu, Q.-X. Guo, *Struct. Chem.* **2005**, *16*, 347–353.

30 R. G. Hicks, *Stable Radicals, Fundamentals and Applied Aspects of Odd-Electron Compounds*, John & Sons ltd, Chichester, GB **2010**.

31 C. A. McFerrin, R. W. Hall, B. Dellinger, *J. Mol. Struc.-THEOCHEM* **2008**, *848*, 16–23.

32 G. Tirzitis, G. Bartosz, *Acta Biochim. Pol.* **2010**, *57*, 139–142.

33 C. Xie, P. M. Lahti, C. George, *Org. Lett.* **2000**, *2*, 3417–3420.

34 M. Miyasaka, T. Yamazaki, E. Tsuchida, H. Nishide, *Macromolecules* **2000**, *33*, 8211–8217.

35 Y. Innami, R. H. L. Kiebooms, T. Koyano, M. Ichinohe, S. Ohkawa, K. Kawabata, M. Kawamatsu, K. Matsuishi, H. Goto, *J. Mater. Sci.* **2011**, *46*, 6556–6562.

36 M. J. Fadden, C. Barckholtz, C. M. Hadad, *J. Phys. Chem. A* **2000**, *104*, 3004–3011.

37 D. R. Albert, H. F. Davis, *J. Phys. Chem. Lett.* **2010**, *1*, 1107–1111.

38 K. Tanaka, M. Ando, Y. Sakamoto, K. Tonokura, *Int. J. Chem. Kinet.* **2011**, *44*, 41–50.

39 B. B. Kirk, D. G. Harman, H. I. Kenttämaa, A. J. Trevitt, S. J. Blanksby, *Phys. Chem. Chem. Phys.* **2012**, *14*, 16719–16730.

40 Z. B. Alfassi, S. Marguet, P. Neta, *J. Phys. Chem.* **1994**, *98*, 8019–8023.

41 R. M. Healy, Y. Chen, I. Kourtchev, M. Kalberer, D. O´Shea, J. C. Wenger, *Environ. Sci. Technol.* **2012**, *46*, 11813–11820.

42 L.-X. Cheng, X.-L. Jin, Q.-F. Teng, J. Cheng, X.-J. Yao, F. Dai, Y.-P. Qian, J.-J. Tang, X.-Z. Li, B. Zhou, *Org. Biomol. Chem*. **2010**, *8*, 1058–1063.

43 P. Lehtovuori, H. Joela, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1928–1933.

44 Y.-J. Shang, Y.-P. Gjan, X.-D. Liu, F. Dai, X.-L. Shang, W.-Q. Jia, Q. Liu, J.-G. Fang, B. Zhou, *J. Org. Chem.* **2009**, *74*, 5025–5031.

45 G.-J. Fan, X.-D. Liu, Y.-P. Qjan, Y.-J. Shang, X.-Z. Li, F. Dai, B. Zhou, Bioorg. *Med. Chem.* **2009**, *17*, 2360–2365.

46 R. S. Borges, G. A. N. Pereira, J. K. L. Vale, L. C. S. Franca, M. C. Monteiro, C. N. Alves, A. B. F. da Silva, *Chem. Biol. Drug Des*. **2013**, *81*, 414–419.

47 A. Tai, T. Sawano, H. Ito, *Biosci. Biotechnol. Biochem.* **2012**, *76*, 314–318.

48 G.-X. Li, Z.-Q. Liu, X.-Y. Luo, *Eur. J. Med. Chem.* **2010**, *45*, 1821–1827.

49 Q. Wang, Y.-P. Qian, F. Dai, D.-L. Lu, W.-J. Yan, Y. Chen, B. Zhou, *Food Chem.* **2013**, *141*, 1259–1266.

50 Y. Rong, Z. Wang, J. Wu, B. Zhou, *Spectrochim. Acta* **2012**, *93*, 235–239.

51 A. Siger, J. Czubinski, P. Kachlicki, K. Dwiecki, E. Lampart-Szczapa, *J. Food Compos. Anal*. **2012**, *25*, 190–197.

52 A. Rubio-Moraga, J. Argandona, B. Mota, J. Perez, A. Verde, J. Fajardo, J. Gomez-Navarro, R. Castillo-Lopez, O. Ahrazem, L. Gomez-Gomez, *J. Ethnopharmacol.* **2013**, *148*, 287–296.

53 M. R. Loizzo, R. Tundis, M. Bonesi, F. Menichini, V. Mastellone, L. Avallone, F. Menichini, *J. Food Compos. Anal*. **2012**, *25*, 179–184.

54 S. P. de Vesser, S. Shaik, *J. Am. Chem. Soc.* **2003**, *125*, 7413–7424.

55 M. J. Zdilla, J. L. Dexheimer, M. M. Abu-Omar, *J. Am. Chem. Soc*. **2007**, *129*, 11505–11511.

56 M. C. Foti, R. Amorati, G. F. Pedulli, C. Daquino, D. A. Pratt, K. U. Ingold, *J. Org. Chem.* **2010**, *75*, 4434–4440.

57 R. Wanke, L. Benisvy, M. L. Kuznetsov, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Chem. Eur. J.* **2011**, *17*, 11882–11892.

58 K. Omura, *J. Org. Chem.*, **2008**, *73*, 858–867.

59 M. Bietti, M. Salamone, *Org. Lett.* **2010**, *12*, 3654–3657.

60 S. Itoh, H. Kumei, S. Nagatomo, T. Kitagawa, S. Fukuzumi, *J. Am. Chem. Soc.* **2001**, *123*, 2165–2175.

61 P. M. Lahti, B. Esat, J. R. Ferrer, Y. Liu, K. A. Marby, C. Xie, C. George, G. Antorrena, F. Palacio, *Mol. Cryst. Liq. Cryst.* **1999**, *334*, 285–294.

62 V. Barone, C. Boilleau, I. Cacelli, A. Ferretti, G. Prampolini, *J. Chem. Theory Comput*. **2013**, *9*, 1958–1963.

63 M. Miyasaka, T. Yamazaki, H. Nishide, *Polym. J.* **2001**, *33*, 849–856.

64 T. Kaneko, H. Abe, M. Teraguchi, T. Aoki, *Macromolecules* **2013**, *46*, 2583–2589.

65 R. D. Webster, *Acc. Chem. Res.* **2007**, *40*, 251–257.

66 Y. Shimazaki, T. Yajima, T. Shiraiwa, O. Yamauchi, *Inorg. Chim. Acta* **2009**, *362*, 2467–2472.

67 F. Thomas, H. Arora, C. Philouze, O. Jarjayes, *Inorg. Chim. Acta* **2010**, *363*, 3122–3130.

68 P. Verma, R. C. Pratt, T. Storr, E. C. Wasinger, T. D. P. Stack, *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 18600–18605.

69 A. Kochem, O. Jarjayes, B. Babtiste, C. Philouze, H. Vezin, K. Tsukidate, F. Tani, M. Orio, Y. Shimazaki, F. Thomas, *Chem. Eur. J.* **2012**, *18*, 1068–1072.

70 I. Garcia-Bosch, X. Ribas, M. Costas, *Chem. Eur. J.* **2012**, *18*, 2113–2122.

71 S. E. Balaghi, E. Safaei, M. Rafiee, M. H. Kowsari, *Polyhedron* **2012**, *47*, 94–103.

72 A. Kochem, L. Chiang, B. Baptiste, C. Philouze, N. Leconte, O. Jarkayes, T. Storr, F. Thomas, *Chem. Eur. J.* **2012**, *18*, 14590–14593.

73 T. Kurahashi, H. Fujii, *J. Am. Chem. Soc.* **2011**, *133*, 8307–8316.

74 A. Kochem, H. Kanso, B. Baptiste, H. Arora, C. Philouze, O. Jarjayes, H. Vezin, D. Luneau, M. Orio, F. Thomas, *Inorg. Chem.* **2012**, *51*, 10657–10571.

75 G. M. Zats, H. Arora, R. Lavi, D. Yufit, L. Benisvy, *Dalton Trans.* **2011**, *40*, 10889–10896.

76 M. J. Ingleson, M. Pink, H. Fan, K. G. Caulton, *J. Am. Chem. Soc.* **2008**, *130*, 4262–4276.

77 E. Matsui, Y. Naruta, F. Tani, Y. Shimazaki, *Angew. Chem. Int. Ed.* **2003**, *42*, 2744–2747.

78 T. Kurahashi, H. Fujii, *J. Am. Chem. Soc.* **2011**, *133*, 8307–8316.

79 T. Jähnert, M. D. Hager, U. S. Schubert, *J. Mater. Chem. A* **2014**, *2*, 15234–15251.

80 O. Piloty, B. G. Schwerin, *Ber. Dtsch. Chem. Gesell.* **1901**, *34*, 1870–1887.

81 P. Hodge, J. E. Gautrot, *Polym. Int.* **2009**, *58*, 261–266.

82 B. Häupler, A. Ignaszak, T. Janoschka, T. Jähnert, M. D. Hager, U. S. Schubert, *Macromol. Chem. Phys.* **2014**, *215*, 1250–1256.

83 T. Le Gall, K. H. Reiman, M. C. Grossel, J. R. Owen, *J. Power Sources* **2003**, *119*, 316–320.

84 K. Oyaizu, Y. Niibori, A. Takahashi, H. Nishide, *J. Inorg. Organomet. Polym.* **2013**, *23*, 243−250.

85 A. E. Murschell, W. H. Kan, V. Thangadurai, T. C. Sutherland, *Phys. Chem. Chem. Phys*. **2012**, *14*, 4626−4634.

86 B. Häupler, R. Burges, T. Janoschka, T. Jähnert, A. Wild, U. S. Schubert, *J. Mater. Chem. A* **2014**, *2*, 8999−9001.

List of abbreviations

AIBN	2,2´-Azobis(*iso*-butyronitrile)
BODIPY	4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene
CAN	Ceric(IV) ammonium nitrate
CNT	Carbon nanotubes
CRP	Controlled radical polymerization
CV	Cyclic voltammetry
Đ	Dispersity
DCC	*N,N´*-Dicyclohexylcarbodiimide
DMF	Dimethylformamide
DMAc	Dimethylacetamide
DMAP	4-Dimethylaminopyridine
DSSC	Dye-sensitized solar cell
ESI	Electrospray ionization
ESR spectroscopy	Electron spin resonance spectroscopy
Fc	Ferrocene
FRP	Free radical polymerization
GC	Gas chromatography
JohnPhos	(2-Biphenyl)di-*tert*-butylphosphine
MALDI	Matrix-assisted laser desorption/ionization
MeOH	Methanol
M_n	Number average molar mass
M_w	Weight average molar mass
MS	Mass spectrometry

$(n\text{-Bu})_4NOH$	Tetra-*n*-butylammonium hydroxide
$(n\text{-Bu})_4NPF_6$	Tetra-*n*-butylammonium hexafluorophosphate
nbd	Norbornadiene
NBS	*N*-Bromosuccinimide
NEt_3	Triethylamine
NMP	*N*-Methylpyrrolidone
NMR spectroscopy	Nuclear magnetic resonance spectroscopy
ORB	Organic radical battery
PC	Propylene carbonate
PMMA	Poly(methyl methacrylate)
PROXYL	2,2,5,5-Tetramethyl-1-pyrrolidinyloxy
PS	Polystyrene
PTFE	Poly(tetrafluoroethylene)
PTMA	Poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate)
PVdF	Poly(vinylidene fluoride)
RAFT	Reversible addition-fragmentation chain transfer
RI	Refractive index
SEC	Size exclusion chromatography
TBAF	Tetra-*n*-butylammonium fluoride
TCAQ	11,11,12,12-Tetracyano-9,10-anthraquinonedimethane
TEMPO	2,2,6,6-Tetramethylpiperidine-1-oxyl
TMEDA	*N*,*N*,*N*′,*N*′-Tetramethylethane-1,2-diamine
THF	Tetrahydrofuran
VGCF	Vapor grown carbon fibers

Curriculum vitae

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Since 01/2016	Sales Engineer at Glatt Ingenieurtechnik GmbH
05/2015 – 12/2015	Looking for new opportunities
12/2011 – 01/2015	Research associate at Friedrich-Schiller-Universität in Jena, research on organic polymer-batteries

Education

10/2011 – 04/2015	Undergraduate studies (part time) in business economics at Friedrich-Schiller-Universität in Jena degree M.Sc.: 2,7
10/2006 – 09/2011	Undergraduate studies in chemistry at Friedrich-Schiller-Universität in Jena with degree diploma: 1,8
09/1997 – 08/2005	High school at Holzlandgymnasiums in Hermsdorf with degree Abitur: 1,9
09/1993 – 08/1997	Elementary school in St. Gangloff

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Publication list

Peer-reviewed publications:

[01] **T. Jähnert**, B. Häupler, T. Janoschka, M. D. Hager, U. S. Schubert “Synthesis and charge-discharge studies of poly(ethynylphenyl)galvinoxyles and their use in organic radical batteries with aqueous electrolytes”, *Macromol. Chem. Phys.* **2013**, *214*, 2616–2623.

[02] **T. Jähnert**, B. Häupler, T. Janoschka, M. D. Hager, U. S. Schubert “Polymers based on stable phenoxyl radicals for the use in organic radical batteries”, *Macromol. Rapid Commun.* **2014**, *35,* 882–887.

[03] **T. Jähnert**, T. Janoschka, M. D. Hager, U. S. Schubert “Polymers with n-type nitroxide side groups: Synthesis and electrochemical characterization”, *Eur. Polym. J.* **2014**, *61*, 105–112.

[04] T. Janoschka, A. Teichler, B. Häupler, **T. Jähnert**, M. D. Hager, U. S. Schubert “Reactive inkjet printing of cathodes for organic radical batteries“, *Adv.Energy Mater.* **2013**, *3*, 1025–1028.

[05] B. Häupler, A. Ignaszak, T. Janoschka, **T. Jähnert**, M. D. Hager, U. S. Schubert “Poly(methacrylates) with pendant benzoquinone units – monomer synthesis, polymerization, and electrochemical behavior: Potential new polymer systems for organic batteries“, *Macromol. Chem. Phys.* **2014**, *215*, 1250−1256.

[06] B. Häupler, R. Burges, T. Janoschka, **T. Jähnert**, A. Wild, U. S. Schubert “PolyTCAQ in organic batteries: Enhanced capacity at constant cell potential using two-electron redox-reactions“, *J. Mater. Chem. A* **2014**, *2*, 8999–9001.

[07] **T. Jähnert**, M. D. Hager, U. S. Schubert “Application of phenolic radicals for antioxidants, as active materials in batteries, magnetic materials and ligands for metal-complexes“, *J. Mater. Chem. A* **2014**, *2*, 15234–15251.

[08] **T. Jähnert**, M. D. Hager, U. S. Schubert “Assorted phenoxyl-radical polymers and their application in lithium-organic batteries”, *Macromol. Rapid Commun.* **2016**, *37*, 725–730.

Oral contributions:

[01] T. Jähnert, T. Janoschka, M. D. Hager, U. S. Schubert “Organic radical batteries“, **BATMAT meeting**, Jena, Germany, October **2012**.

[02] T. Jähnert, T. Janoschka, M. D. Hager, U. S. Schubert “Organic radical batteries“, **BATMAT meeting**, Chemnitz, Germany, May **2013**.

[03] T. Jähnert, T. Janoschka, M. D. Hager, U. S. Schubert “Organic radical batteries“, **BATMAT meeting**, **Schreiner Group GmbH & Co. KG**, Oberschleißheim, Germany, October **2013**.

[04] T. Jähnert, T. Janoschka, M. D. Hager, U. S. Schubert “Organic radical batteries“, **BATMAT meeting**, **Felix Schöller Holding GmbH & Co. KG**, Freiberg, Germany, March **2014**.

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Declaration of authorship / Selbstständigkeitserklärung

Ich erkläre, dass ich die vorliegende Arbeit selbständig und unter Verwendung der angegebenen Hilfsmittel, persönlichen Mitteilungen und Quellen angefertigt habe.

I certify that the here presented work is, to the best of my knowledge, original and the results of my own investigations, except as acknowledged, and has not been submitted, either in part or whole, for a degree at this or any other university.

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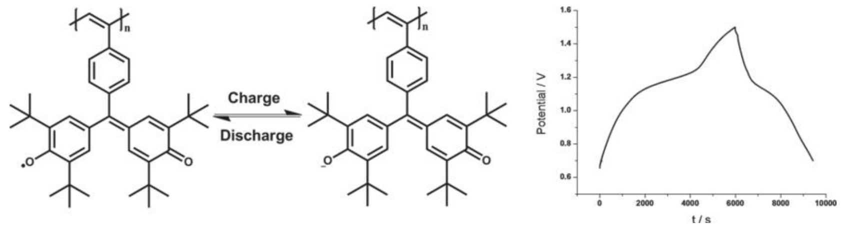
Thomas Jähnert

Publications P1-P8

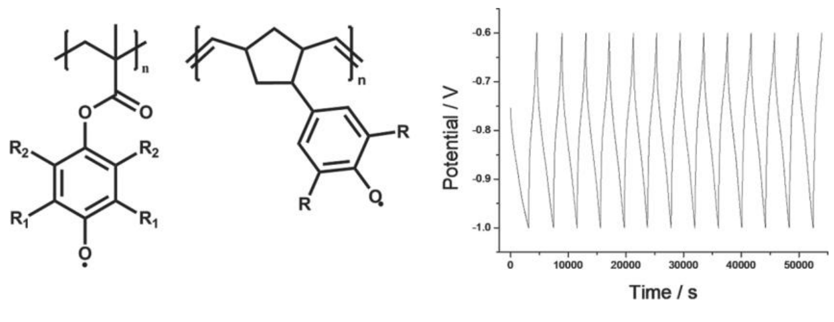
Graphical Abstracts

P1 “Synthesis and charge-discharge studies of poly(ethynylphenyl)galvinoxyles and their use in organic radical batteries with aqueous electrolytes”



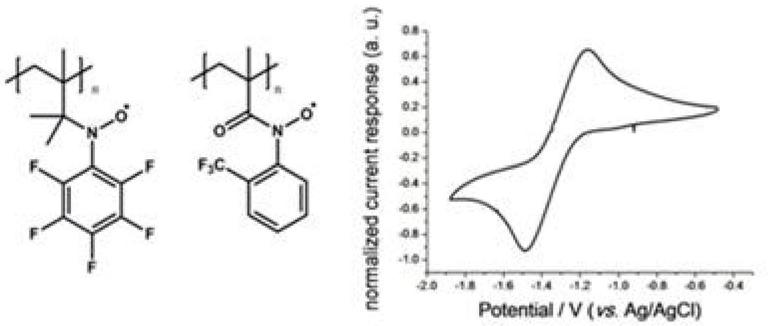
The synthesis and electrochemical characterization of polymers that bear galvinoxyles in the side chains is described. The monomers are synthesized employing C–C coupling reactions, polymerized with Rh(nbd)BPh$_4$ as a catalyst, and subsequently oxidized. These galvinoxyl-containing polymers represent interesting anode materials for organic radical batteries and employ stable organic radicals, which are bound to polymers; hereby, metals and metal oxides, as active compounds, can be replaced. With the use of ethynylphenyl-galvinoxyles as anode-active material and poly(2,2,6,6-tetramethylpiperidine-*N*-oxyl)methacrylate (PTMA) as cathode-active material, metal-free batteries with an aqueous and environment-friendly electrolyte are built. These cells are tested for their charge and discharge capacities.

P2 “Polymers based on stable phenoxyl radicals for the use in organic radical batteries”



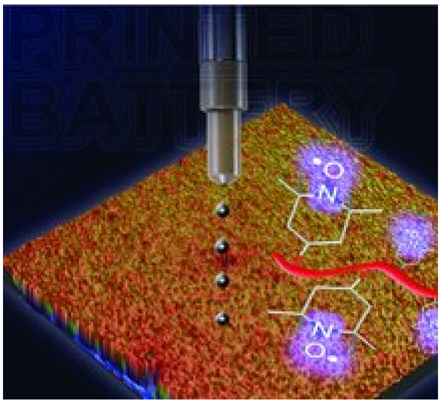
Polymers with pendant phenoxyl radicals are synthesized and the electrochemical properties are investigated in detail. The monomers are polymerized using ring-opening metathesis polymerization (ROMP) or free-radical polymerization methods. The monomers and polymers, respectively, are oxidized to the radical either before or after the polymerization. These phenoxyl radicals containing polymers reveal a reversible redox behavior at a potential of −0.6 V (vs Ag/AgCl). Such materials can be used as anode-active material in organic radical batteries (ORBs).

P3 “Polymers with n-type nitroxide side groups: Synthesis and electrochemical characterization”



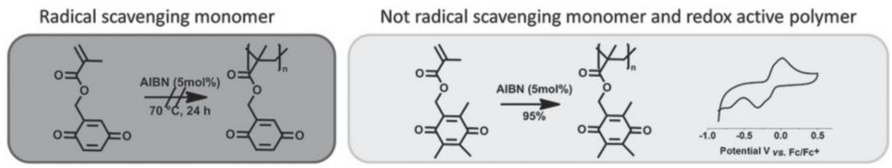
The synthesis and electrochemical characterization of nitroxide-bearing polymers with electron-withdrawing substituents is described. Styrene- and methacrylamide-monomers were polymerized employing free-radical polymerization techniques and subsequently oxidized. *iso*-Butylene monomers were polymerized in their oxidized form *via* cationic polymerization. These polymers were tested with cyclic voltammetry for their redox-stability and potential. They revealed reversible redox-reactions at potentials of −1.28 V (*vs.* Fc/Fc$^+$) and below.

P4 *“*Reactive inkjet printing of cathodes for organic radical batteries“



Inkjet printing can be used to manufacture flexible organic radical battery (ORB) electrodes. A reactive printing approach based on the thermal crosslinking of amine bearing redoxactive radical polymers is developed. The printed electrodes are stable for over one hundred charging/discharging cycles.

P5 “Poly(methacrylates) with pendant benzoquinone units – monomer synthesis, polymerization, and electrochemical behavior: Potential new polymer systems for organic batteries“

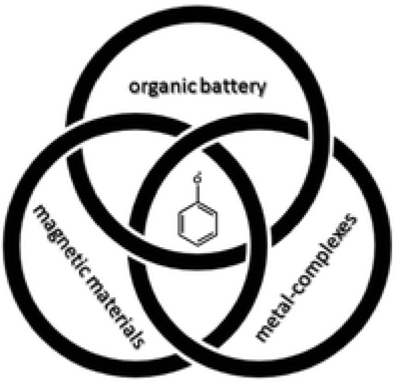


Redox-active polymers became the focus of attention in the field of organic electronics during the last decade. Quinoide systems are intensively studied in this field. Although benzoquinones are generally known as radical scavengers, certain monomers can be polymerized by radical polymerization techniques. For this purpose, methacrylate functionalities are attached to the redox-active quinone moiety. A free-radical polymerization technique is applied utilizing AIBN as initiator. The molar mass can be adjusted by the choice of an appropriate solvent system. Electrochemical investigations of these new monomers and polymers, in particular cyclic voltammetry, are performed in aqueous and non-aqueous electrolytes in the dissolved and solid states, showing the potential usefulness of the system for applications in organic radical batteries.

P6 “PolyTCAQ in organic batteries: Enhanced capacity at constant cell potential using two-electron redox-reactions“

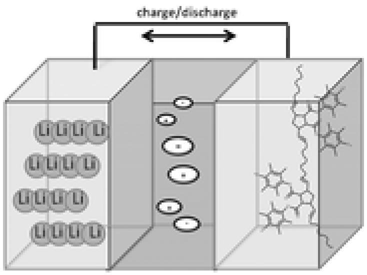
The application of polymers bearing tetracyano-9,10-anthraquinonedimethane (TCAQ) units as electrode materials in organic batteries enables one narrow charge discharge plateau due to the one two-electron-redox-reaction of the TCAQ core. Li-organic batteries manufactured with this polymer display repeatable charge–discharge characteristics associated with a capacity of 156 mA h g^{-1} and a material activity of 97%.

P7 “Application of phenolic radicals for antioxidants, as active materials in batteries, magnetic materials and ligands for metal-complexes“



Organic radicals originating from phenolic compounds have been known for decades. The most well-known of these radical species are the phenoxyl-radical and the galvinoxyl-radical. Those radicals are characterized by the unpaired electron at a formerly phenolic oxygen-atom. In natural systems phenolic radicals are often found as intermediate products or as part of antioxidant and radical-scavenging processes. Tyrosyl-radicals or tocopherol-radicals represent typical examples. More reactive radicals like the hydroxyl-radical come in contact with these compounds and react to harmless water, while the radical is passed to the phenolic compound. Other radical scavengers in biological systems are, *e.g.*, flavonoid molecules like catechin, luteolin and quercetin as well as resveratrol, vanillin or neurotransmitters like dopamine and epinephrine. In organic radical batteries phenoxyl-radicals or galvinoxyl-radicals can play a pivotal role as electroactive material to store electric energy. They are also often investigated for their magnetic properties, or their redox-activity when used in metal-complexes. From the tyrosyl-radical as part of enzymes to galvinoxyl as dopant in organic solar cells phenolic radicals display great versatility in structure and function. This review summarizes the application of phenol-based radicals in biological as well as artificial materials and systems over the last years.

P8 “Assorted phenoxyl-radical polymers and their application in lithium-organic batteries”



The synthesis and electrochemical characterization of novel polymers bearing phenoxyl-radicals as redox-active side chains is described. The monomers are synthesized from the corresponding phenols and quinones, respectively. These compounds are subsequently polymerized via ring-opening metathesis polymerization. The electrochemical properties of the phenoxyl-radical polymers are characterized using cyclic voltammetry and the most promising polymer is investigated as active material in a lithium coin-cell, creating the first phenoxyl-lithium battery. These phenoxyl-containing polymers represent interesting anode materials for organic radical and lithium batteries due to their suitable redox-potentials and possibility to create batteries with higher potentials as well as straightforward synthesis procedures.

Publication P1

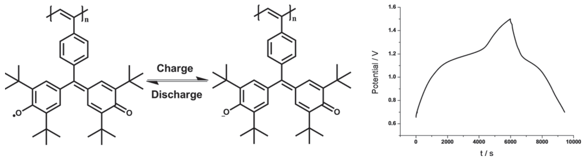
“Synthesis and charge - discharge studies of poly(ethynylphenyl)galvinoxyles and their use in organic radical batteries with aqueous electrolytes”

T. Jähnert, B. Häupler, T. Janoschka, M. D. Hager, U. S. Schubert, *Macromol. Chem. Phys.* **2013**, *214*, 2616−2623.

Synthesis and Charge–Discharge Studies of Poly(ethynylphenyl)galvinoxyles and Their Use in Organic Radical Batteries with Aqueous Electrolytes

Thomas Jähnert, Bernhard Häupler, Tobias Janoschka, Martin D. Hager, Ulrich S. Schubert*

The synthesis and electrochemical characterization of polymers that bear galvinoxyles in the side chains is described. The monomers are synthesized employing C–C coupling reactions, polymerized with Rh(nbd)BPh_4 as a catalyst, and subsequently oxidized. These galvinoxyl-containing polymers represent interesting anode materials for organic radical batteries and employ stable organic radicals, which are bound to polymers; hereby, metals and metal oxides, as active compounds, can be replaced. With the use of ethynylphenyl-galvinoxyles as anode-active material and poly(2,2,6,6-tetramethylpiperidine-*N*-oxyl)methacrylate (PTMA) as cathode-active material, metal-free batteries with an aqueous and environment-friendly electrolyte are built. These cells are tested for their charge and discharge capacities.



1. Introduction

Organic radical batteries (ORBs) have gained more and more attention in recent years, because of the need for a cheap, metal-free energy-storage system.[1] ORBs can be rapidly charged and discharged through the reversible oxidation and reduction of stable organic radicals.[2] They show an excellent cycle life of 1000 cycles and beyond.[2–4] Smaller and cheaper energy sources can be used for electronic applications like biochips, smart packages, and sensors. Because of their long cycle life, ORBs could be utilized in such systems for months or years without significant capacity loss.[5]

Cathode materials for ORBs have been extensively studied; currently, the 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) radical combined with various polymer backbones is still the material of choice.[4,6,7] Because of its stability, easy synthesis of functional polymers and price, it is the preferred active material for cathodes in ORBs. Unfortunately, TEMPO cannot be employed as an anode-active material, because the reduction to the aminoxyl anion is irreversible.[8]

In contrast, only few promising anode materials for ORBs have been reported up to now. Amongst others, the most studied compounds with a negative redox potential are based on the stable galvinoxyl[9,10] (Scheme 1) and verdazyl radicals[11] as well as viologene[4] derivatives. Additionally, nitronyl–nitroxides that perform as both *p*- and *n*-type active material can also be used as anode materials.[12,13]

Galvinoxyles have so far been synthesized with different substituents and polymerizable groups,[14–17] but only the styrene-based poly[(*p*-vinylphenyl)galvinoxyl][18]

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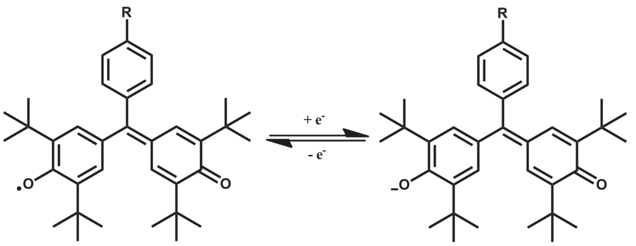


Scheme 1. Schematic representation of oxidation and reduction of galvinoxyles.

has been applied as anode material for ORBs.[1,9,10,12] Apart from being employed in ORBs, galvinoxyles have also been used as building component for purely organic magnetic materials[16] and for their optical and magnetic properties in general.[17] Because galvinoxyles are stable, persistent, and easy to handle radicals, they have been frequently used for their magnetic properties.[9,14–17]

We have explored the use of galvinoxyles with poly(acetylene) backbones as redox-active materials for ORBs with aqueous electrolytes and examined the charge and discharge behavior. Moreover, the fabrication of a composite electrode consisting of active polymer, graphite, and vapor-grown carbon fibers (VGCF) and the assembly and charge–discharge behavior of an all-organic radical battery in combination with poly(2,2,6,6-tetramethylpiperidine-*N*-oxyl)methacrylate (PTMA) as cathode material utilizing an aqueous electrolyte has been studied.

2. Experimental Section

2.1. Materials

All the organic reactions were performed under a nitrogen atmosphere. All the used chemicals and solvents were purchased from Sigma–Aldrich, Acros Organics, Apollo Scientific, and Alfa Aesar, and were used without further purification unless otherwise specified. Unless otherwise noted, solvents were dried according to standard procedures. Dry tetrahydrofuran (THF) and toluene were obtained from a Pure Solv MD-4-EN solvent purification system. (4-Bromo-2,6-di-*tert*-butylphenoxy)trimethylsilane,[19] poly(2,2,6,6-tetramethylpiperidin-4-yl methacrylate),[20] poly(TEMPO-methacrylate),[6] and Rh(nbd)BPh_4[21] were synthesized according to procedures described in the literature.

2.2. General Procedures

Reactions were monitored by thin layer chromatography (TLC) (aluminum sheets coated with silica gel 60 F254 by Merck) and size-exclusion chromatography (SEC) (using a Shimadzu SCL-10A VP controller, a LC-10AD pump, a RID-10A refractive index detector, a SPD-10AD VP UV-detector and a PSS SDV pre/lin S column; temperature: 40 °C, eluent: chloroform:triethylamine:*iso*-propanol 94:4:2; flow rate: 1 mL min^{-1}, calibration: polystyrene).

SECs for the radical polymers were measured with a Shimadzu SCL-10A VP controller, a LC-10AD pump, a RID-10A refractive index detector, a SPD-10AD VP UV-detector, and a PSS SDV pre/lin M (THF-N) column; temperature: 40 °C, eluent: THF; flow rate: 1 mL min^{-1}, calibration: polystyrene.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 250 (250 MHz) and a Bruker AC 300 (300 MHz) spectrometer at 298 K. Chemical shifts are reported in parts per million (ppm, δ scale) relative to the residual signal of the deuterated solvent.

Column chromatography was performed on silicagel 60 (Merck). Elemental analyses were carried out using a Vario ELIII–Elementar Euro and an EA–HekaTech.

Electrochemical measurements were performed on a Princeton Applied Research Versastat potentiostat with a standard three-electrode configuration using a graphite-disk working electrode, a platinum-rod auxiliary electrode, and an Ag/AgCl reference electrode. Ferrocene was used as internal standard (0.384 V vs Ag/AgCl). The experiments were carried out in degassed solvents containing tetra-*n*-butylammonium hexafluorophosphate salt (0.1 M). At the end of each measurement, ferrocene was added as an internal standard.

2.3. Synthesis of Methyl 4-Ethynylbenzoate (1)

Methyl 4-bromobenzoate (12.0 g, 55.0 mmol), trimethylsilylacetylene (6.6 g, 67.0 mmol), triethylamine (15 mL, 111.0 mmol), and bis(triphenylphosphino) palladium(II) dichloride (2.2 g, 3.2 mmol, 6 mol%) were dissolved in 150 mL THF and purged with nitrogen for 40 min. Subsequently, CuI (1.1 g, 6.1 mmol, 11 mol%) was added and the mixture was stirred for 16 h at room temperature. The solution was concentrated under vacuum and then extracted with 100 mL chloroform and washed with 100 mL water as well as 80 mL brine. The organic phase was dried over $MgSO_4$ and the solvent was completely evaporated under reduced pressure. The residue was dissolved in 50 mL THF and tetra-*n*-butylammonium fluoride 1 M in THF (10 mL, 0.0122 mol) was added and stirred for 1 h. The solution was concentrated and purified over a short pad of silica (Silica 60; ethyl acetate) to yield a brown powder of **1** [8.13 g (92%)].

^{1}H NMR (250 MHz, $CDCl_3$, δ): 8.01 (d, J = 6.7 Hz, 2 H), 7.57 (d, J = 6.7 Hz, 2 H), 3.92 (s, alkyne CH, 1 H), 3.23 (s, OCH_3, 3 H). ^{13}C NMR (60 MHz, $CDCl_3$, δ): 52.4 (OCH_3), 83.3 (CH), 84.2 (C alkyne), 123.9 (C aromatic), 128.5 (2 C aromatic), 130.5 (C aromatic), 132.0 (2 C aromatic), 165.6 (COO). Anal. calcd for $C_{10}H_8O_2$: C 74.99, H 5.03; found: C 75.03, H 4.79.

2.4. Synthesis of Methyl 3,5-Dibromobenzoate (2)

Sulfuric acid (0.1 mL, 1.8 mmol) was added to a solution of 3,5-dibromobenzoic acid (3.00 g, 10.7 mmol) dissolved in 50 mL methanol and the solution was stirred under reflux for 5 h. After cooling, the solution was extracted with 50 mL water and 50 mL CH_2Cl_2. The organic phase was subsequently washed with 50 mL 10% aq. Na_2CO_3 and 50 mL water.

Drying over Na_2SO_4 and subsequent removal of the solvent at reduced pressure yielded a white powder of **2** (2.79 g, 89%).

^{1}H NMR (250 MHz, $CDCl_3$,δ): 8.08 (s, 2 H), 7.82 (s, 1 H), 3.91 (OCH_3, s, 3 H). ^{13}C NMR (60 MHz, $CDCl_3$, δ): 52.3 (OCH_3), 111.7

(2 C aromatic), 137.6 (2 C aromatic), 147.7 (C aromatic), 148.2 (C aromatic). Anal. calcd for $C_8H_6Br_2O_2$: C 32.69, H 2.06, Br 54.37; found: C 32.55, H 1.97, Br 54.15

2.5. Synthesis of Methyl 3,5-Diethynylbenzoate (3)

To a solution of **2** (2.50 g, 8.8 mmol), trimethylsilylacetylene (2.00 g, 20.0 mmol) and triethylamine (3 mL, 22.0 mmol) in 50 mL THF bis(triphenylphosphino)-palladium(II) dichloride (0.25 g, 0.35 mmol, 4 mol%) were added and the reaction mixture was purged with nitrogen for 45 min. CuI (0.13 g, 0.7 mmol, 8 mol%) was added under nitrogen protection and the reaction mixture was stirred for 3 d at 25 °C. 50 mL chloroform and 50 mL water were added. The organic phase was washed with 30 mL brine, dried over $MgSO_4$ and, subsequently, the solvent was removed under reduced pressure. The residue dissolved in 50 mL THF and tetrabutylammonium fluoride (TBAF) (3.0 g, 11.0 mmol) was added and the mixture was stirred for 2 h. The solvent was evaporated at reduced pressure and the residue extracted with 60 mL chloroform and 60 mL water. The organic phase was washed with 50 mL brine. Drying over $MgSO_4$, removal of the solvent at reduced pressure and subsequent washing over a short pad of silica (Silica 60; ethyl acetate) gave **3** as light brown powder (1.52 g, 87%).

^1H NMR (250 MHz, $CDCl_3$, δ): 8.35 (s, 2 H), 7.66 (s, 1 H), 3.93 (s, OCH_3, 3 H), 3.81 (s, CH, 2 H). ^{13}C NMR (60 MHz, $CDCl_3$, δ): 52.2 (OCH_3), 82.9 (2CH), 83.7 (2 C alkyne), 114.4 (2 C aromatic), 134.5 (C aromatic), 138.5 (2 C aromatic), 146.0 (C aromatic), 165.4 (COO). Anal. calcd for $C_{12}H_8O_2$: C 78.25, H 4.38; found: C 78.45, H 4.43. ESI-MS m/z (%): 184 (60) [M^+], 169 (100) [$M^+ - CH_3$].

2.6. Synthesis of (*p*-Ethynylphenyl)hydrogalvinoxyl (4)

n-BuLi 1.6 M in hexane (15.6 mL, 25 mmol) was added dropwise to a solution of (4-bromo-2,6-di-*tert*-butylphenoxy)trimethylsilane (7.5 g, 21 mmol) in 100 mL THF at –78 °C. After 30 min, stirring **1** (1.68 g, 11 mmol) and tetramethylethylenediamine (TMEDA) (4.0 mL, 27 mmol) in 15 mL THF were added. The solution was allowed to warm to room temperature over 3 h. KOH (6.00 g, 11 mmol) dissolved in 20 mL water was poured into the solution and the whole mixture was stirred overnight. 50 mL aq. 10% NH_4Cl was added, which was subsequently extracted with 150 mL chloroform. Then, the organic phase was washed with 100 mL water and dried over Na_2SO_4. The solvent was removed under reduced pressure. Subsequently, the remaining compounds were purified by column chromatography (Silica 60, dichloromethane:*n*-hexane 10:1), which gave **4** as orange powder (2.84 g, 52%). The compound was stored under nitrogen to prevent oxidation.

^1H NMR (250 MHz, $CDCl_3$, δ): 8.01 (d, J = 8.3 Hz, 2 H), 7.56 (d, J = 8.3 Hz, 2 H), 7.10 (s, 2 H), 7.01 (s, 2H), 5.53 (s, OH, 1 H), 3.92 (s, CH, 1 H), 2.17 (s, CH_3, 36 H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$, δ): 30.1 (6 CH_3), 30.3 (6 CH_3), 34.3 (2 $\underline{C}(CH_3)_3$), 34.5 (2 $\underline{C}(CH_3)_3$), 78.5 (CH), 82.0 (C alkyne), 122.3 (2 C aromatic), 124.9 (C aromatic), 127.9 (2 C aromatic), 129.9 (C aromatic), 132.2 (2 C aromatic), 135.6 (2 C aromatic), 135.7 (C aromatic), 135.9 (2 C aromatic), 138.2 (2 C aromatic), 141.5 (C aromatic), 147.3 (C aromatic), 152.9 (C4), 154.6 (COH aromatic), 186.5 (C=O aromatic). Anal. calcd for $C_{37}H_{46}O_2$: C 85.01, H 8.87; found: C 84.88, H 8.93. MALDI-MS m/z: 545 [$M + Na^+$]

2.7. Synthesis of (3,5-Diethynylphenyl)hydrogalvinoxyl (5)

(4-Bromo-2,6-di-*tert*-butylphenoxy)trimethylsilane (2.94 g, 80 mmol) was dissolved in 50 mL THF and cooled to –78 °C under nitrogen. *n*-BuLi 1.6 M in hexane (6 mL, 10 mmol) was added dropwise. After 30 min of stirring **3** (0.70 g, 3.5 mmol) and TMEDA (3 mL, 20 mmol) in 15 mL THF were added an d the solution was stirred 2 h at –78 °C and additionally at room temperature overnight. KOH (4.08 g, 7 mmol) in 30 mL MeOH was added to the mixture, which was then stirred overnight. 50 mL 10% aq. NH_4Cl was added and after stirring for 30 min, extraction with 100 mL diethyl ether was performed. The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The remaining compounds were purified by column chromatography (Silica 60, dichloromethane:hexane 1:1) gave **5** as an orange powder (1.2 g, 56%). The compound was stored under nitrogen to prevent oxidation.

^1H NMR (250 MHz, $CDCl_3$, δ): 7.82 (s, 2 H), 7.51 (s, 1 H), 7.01 (s, 2 H), 6.98 (s, 2H), 5.53 (s, OH, 1 H), 3.76 (s, CH, 2 H), 1.48 (s, CH_3, 36 H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$, δ): 29.5 (6 CH_3), 29.7 (6 CH_3), 34.4 (2 $\underline{C}(CH_3)_3$), 35.3 (2 $\underline{C}(CH_3)_3$), 78.8 (2 CH), 83.4 (2 C alkyne), 122.7 (2 C aromatic), 129.1 (C aromatic), 130.0 (2 C aromatic), 131.5 (2 C aromatic), 132.0 (C aromatic), 132.2 (2 C aromatic), 132.5 (C aromatic), 135.4 (2 C aromatic), 141.8 (2 C aromatic), 146.9 (C aromatic), 147.0 (C aromatic), 155.5 (C4), 156.7 (COH aromatic), 186.1 (C=O aromatic). Anal. calcd for $C_{39}H_{46}O_2$: C 85.67, H 8.48; found: C 85.39, H 8.26. MALDI-MS m/z: 570 [$M + Na^+$]

2.8. General Procedure of the Polymerization of Ethynyl Monomers

The applied reaction conditions are summarized in Table 1. A glass polymerization tube was charged with ethynyl monomer **4** or **5** and catalyst (10 mol%) in THF (0.2 M). The solutions were purged for 30 min with nitrogen. The polymerization was carried out by stirring at room temperature for 48 h. The reaction mixture was precipitated in hexane to give a yellow polymer.

NMR spectroscopy characterization of polymers:

4-polymerized:

^1H NMR (300 MHz, $CDCl_3$, δ): 7.34 (b, ArH), 7.02–7.44 (b, ArH), 5.50 (b, OH), 5.42 (b, CH), 2.04–1.88 (b, α-CH_2), 1.05–1.45 (b, CH_3) ppm.

5-polymerized:

^1H NMR (300 MHz, $CDCl_3$, δ): 7.20 (b, ArH), 7.54–7.73 (b, ArH), 5.56 (b, OH), 5.41 (b, CH), 2.11–1.85 (b, α-CH_2), 0.98–1.40 (b, CH_3) ppm.

2.9. General Procedure for the Oxidation of the Polymers

Oxidation of the polymers was carried out as follows: A solution of the poly(acetylene) in toluene (0.5 M) was purged with nitrogen for 30 min. PbO_2 (excess) was added and this suspension was stirred for 2 h. After filtration and subsequent concentration of the solution under reduced pressure, the residue was reprecipitated in hexane to give a red polymer.

Table 1. Conditions for polymerization of ethynyl monomers.

Monomer	Catalyst	$\bar{M}_n$ [a)] [g mol^{-1}]	$\bar{M}_w$ [a)] [g mol^{-1}]	PDI	Yield [%]
4	$Rh(nbd)_2BF_4$	1400	2200	1.57	40
4	$Rh(nbd)BPh_4$	5300	9700	1.85	50
4	$Rh(nbd)BPh_4 + NEt_3$	3500	10 400	2.97	80
5	$Rh(nbd)_2 BF_4$	–	–	–	–
5	$Rh(nbd)BPh_4$	9400	39 100	4.17	70
5	$Rh(nbd)BPh_4 + NEt_3$	13 100	54 600	4.18	85

[a)] Determined by SEC ($CHCl_3$, PS calibration).

2.10. Fabrication of Radical Polymer/Graphite/VGCF Composite Electrode

Polymer/graphite/VGCF composite electrodes were fabricated by using the following method. Radical-containing polymer (10 mg), graphite (56 mg) and VGCF (24 mg) as conductive additives, and PVDF (10 mg) as binder were carefully grounded in a mortar. *N*-Methyl-2-pyrrolidone was added to give a paste. This was kneaded further using a mortar and more *N*-methyl-2-pyrrolidone was added to prevent drying. Subsequently, the paste was bladed on a graphite sheet using a steel template (area: 1.5 cm^2). The fabricated electrodes were dried under reduced pressure at 40 °C overnight.

2.11. CV Measurements

CV measurements were performed in a voltage range of (–1) to 1 V (vs Ag/AgCl) using 0.1 M Bu_4NPF_6 in DMF as the electrolyte. An Ag/AgCl electrode was used as the reference, Pt metal as the counter electrode and glassy carbon as the working electrode. The measurements were performed at a scan rate of 100 mV s^{-1}.

2.12. Half-Cell Measurements

Half-cell measurements were performed using the fabricated electrodes. Before measurements, the electrodes were stored for 24 h in a solution of 0.1 M NaCl in water. A 0.1 M solution of NaCl in water was used as electrolyte, Ag/AgCl as counter electrode, Pt metal as counter electrode, and the fabricated electrodes as working electrodes. Charge and discharge measurements were performed under nitrogen atmosphere.

2.13. Assembly of an Organic Radical Battery

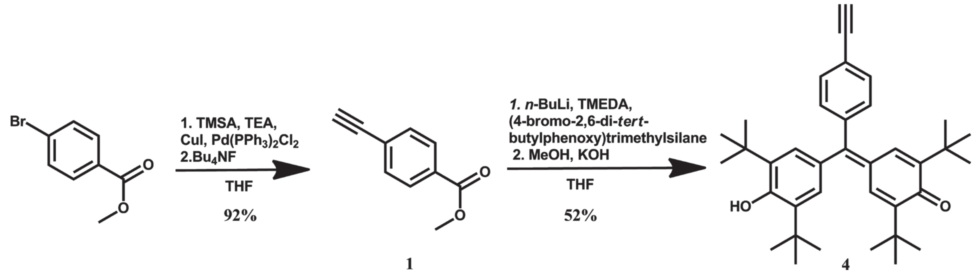
Electrodes were prepared with PTMA for the cathode and with poly(4-ethynylphenyl)galvinoxyl for the anode. Radical-containing polymer (30 mg), graphite (168 mg) and VGCF (72 mg) as conductive additives, as well as PVDF (30 mg) as binder were used according to the mentioned procedure to fabricate a paste, which was spread on a graphite sheet (4 cm^2) using a doctor blade method. A small uncoated strip of graphite (3 × 0.5 cm) was used to contact the electrodes. The fabricated electrodes were dried under reduced pressure at 40 °C overnight (electrode composition: radical polymer 10 wt%, graphite 56 wt%, VGCF 24 wt%, and PVDF 10 wt%). The electrodes were placed on a polyethylene foil, so that their contact pieces were on opposite sides. A polyester separator was placed on one electrode. The foil was carefully folded, that the electrodes would be on top of each other with the separator between. Three sides were heat sealed with a commercial heat sealer. Through the remaining opening 0.1 M aq. NaCl as electrolyte was injected. Remaining air in the cell was removed and the battery was completely sealed.

3. Results and Discussion

3.1. Synthesis and Characterization

(*p*-Ethynylphenyl)hydrogalvinoxyl **4** was synthesized in a straightforward manner and in high yields starting with commercially available methyl-4-bromobenzoate. First, the polymerizable alkyne group was introduced by a Sonogashira reaction and subsequent the protecting group was removed using tetrabutylammonium fluoride to form the alkyne **1**. (4-Bromo-2,6-di-*tert*-butylphenoxy)trimethylsilane was treated first with *n*-BuLi followed by an addition of alkyne **1** and a deprotection of the TMS group during the alkaline purification step to form (*p*-ethynylphenyl)hydrogalvinoxyl **4** (Scheme 2). The yield of this synthesis is comparable to the synthesis of other reported galvinoxyles.[14] In comparison to the synthesis of (*p*-vinylphenyl)hydrogalvinoxyl, (*p*-ethynylphenyl)hydrogalvinoxyl **4** is more efficient to synthesize, because only two reaction steps are required instead of four for the styrene derivative. The following polymerization of the polymer is also less hindered by formed galvinoxyl radicals, which can be formed through oxidation with air (Figure 1).

This synthetic route was chosen because the direct introduction of the alkyne group at (*p*-bromophenyl) hydrogalvinoxyl[16] was unsuccessful under various conditions. The introduction of the alkyne group via the Sonogashira reaction led in this case only to the recovery



Scheme 2. Schematic representation of the synthesis of monomer **4**.

of the starting material (*p*-bromophenyl)hydrogalvinoxyl. The reaction may be hindered through the bulkiness of the bromine derivative, which can hinder the transmetallation step during the catalysis cycle. Temperature ranges from room temperature up to 80 °C were tested and several Pd catalysts were employed; however, the formation of the desired product could not be observed.

The bisethynyl compound **5** was synthesized starting with commercially available 3,5-dibromobenzoic acid, which was in the first step esterificated with methanol to form 3,5-dibromobenzoate **2** under acidic conditions. A Sonogashira reaction with trimethylsilyl-acetylene followed by an in situ deprotection step using tetrabutylammonium fluoride yielded methyl 3,5-diethynylbenzoate **3** (Scheme 3). The double substituted monomer **5** was synthesized under similar conditions as described for the monosubstituted building block. (4-Bromo-2,6-di-*tert*-butylphenoxy)trimethylsilane was treated with *n*-BuLi. To this solution, methyl 3,5-diethynylbenzoate **3** was added, followed by an alkaline treatment for deprotection of the trimethylsilyl groups to form (3,5-diethynylphenyl) hydrogalvinoxyl **5**. Formation of the galvinol compound during the reaction could be observed through color change. Like most triphenylmethane derivatives, galvinoles also possess intense coloration, which changes according to the pH value of the solution. The yield of this synthesis is with 56% again comparable to the reported literature examples of hydrogalvinoxyles.[14] In contrast to the monosubstituted galvinoles, no double-substituted galvinol with vinyl groups is known so far.

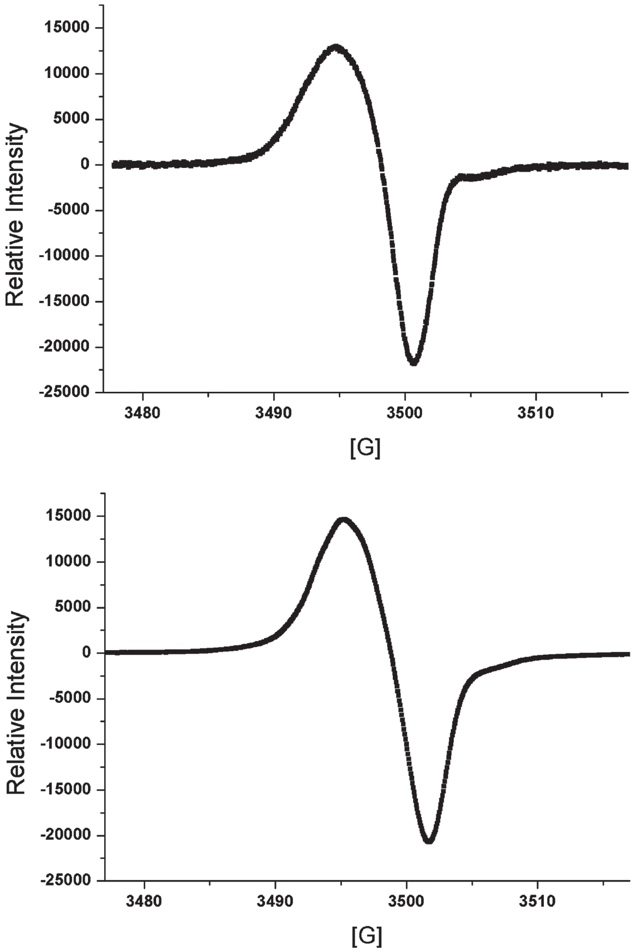
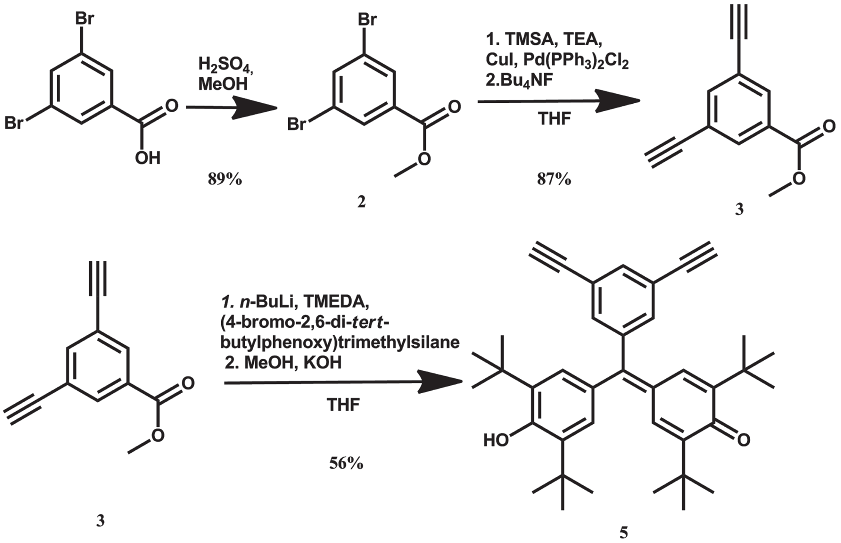
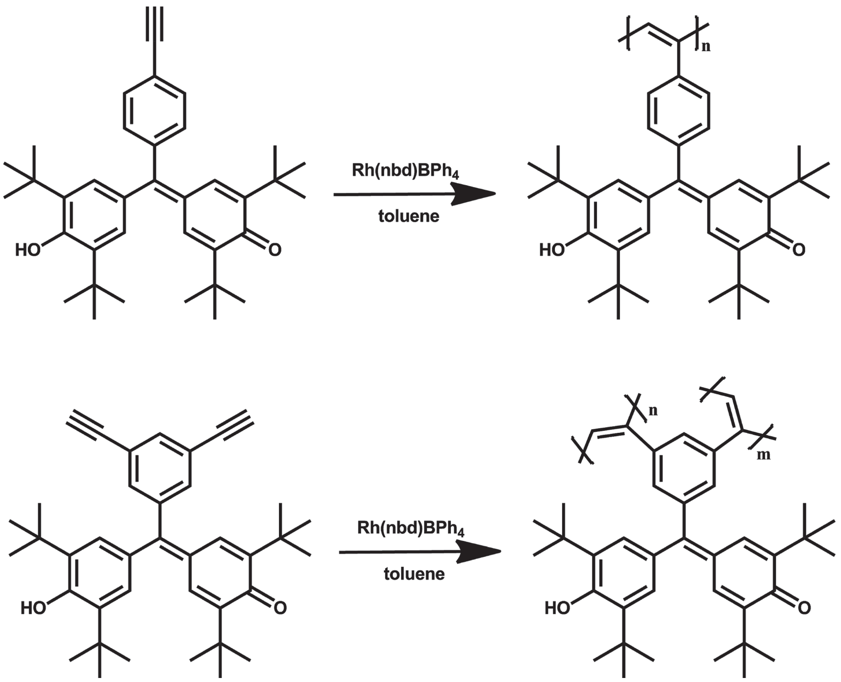


Figure 1. Electron spin resonance (ESR) of radical-containing polymer derived from monomer **4** (top) and **4** after 1 month under air (bottom).

Both acetylene monomers were used for polymerization experiment. For this purpose, several catalysts were tested for the polymerization of the ethynyl-bearing monomers. Rh(nbd)BPh$_4$[21] was found to be the most effective catalyst (Scheme 4). Other tested catalysts like Rh(nbd)$_2$BF$_4$ only led to low molar mass oligomers with very low yields (Table 1). Polymers obtained by the polymerization of **4** with Rh(nbd)BPh$_4$ revealed a molar mass of $\overline{M}_n$: 5000 g mol^{-1} with polydispersity index (PDI) values between two and three and were soluble in most common organic solvents. Also acetylene polymers derived from monomer **5** were synthesized. Molar masses of $\overline{M}_n$: 13 000 g mol^{-1} were achieved with high PDI values of four. The solubility of the polymers on the basis of monomer **5** is lower than the previous one, but also this polymer class is still soluble in most organic solvents after several minutes of stirring. This was observed in solubility tests with acetonitrile and concentrations of 10–50 mg mL^{-1}. The oxidation of the polymers was performed with PbO$_2$.[14] Also tested were potassium hexacyanoferrate(III)[14] and H$_2$O$_2$/Na$_2$WO$_4$,[20] but PbO$_2$ proved to be the most effective and easiest to use with a simple purification procedure.



Scheme 3. Schematic representation of the synthesis of monomer **5**.



Scheme 4. Schematic representation of the coordination polymerization of ethynyl monomers **4** (top) and **5** (bottom).

ESR spectroscopy proved the existence of the radical (Figure 1) with a *g*-value of 2.0038 and the radical concentration could be determined through the spin concentration to be roughly 70%. This value is in good accordance to other reported oxidations of polymeric galvinoles.[14] After the oxidations, the molar masses and PDI values of all polymers increased due to side reactions caused by the formed radicals. The molar masses of the monofunctionalized galvinoxyl after oxidation were in the range of $\overline{M}_n$ 15 000 g mol^{-1} with PDIs around four. Molar masses of the bisfunctionalized galvinoxyl after oxidation could be measured to $\overline{M}_n$: 50 000 g mol^{-1} (PDI > 6).

3.2. Electrochemistry

Additionally, the redox behavior of the polymers was studied. Cyclic voltammograms revealed reversible redox reactions at −0.40 V (vs Fc/Fc$^+$), which are comparable to the literature values of galvinoxyles[1] (Figure 2) and smaller satellite signals, which can be attributed to redox reactions of the polyacetylene backbone.[22] The electrochemical stability of the polymers was examined by CV measurements over 50 cycles. Both polymers revealed a stable redox behavior and could therefore subsequently be tested as active anode material in ORBs.

A 0.1 M aqueous solution of NaCl with 0.01 M tetrabutylammonium hydroxide proved to be the most appropriate as electrolyte for charge–discharge experiments of the half-cell, because of its conductivity, the insolubility of the polymers and also their swelling in the electrolyte. The fabricated electrodes were allowed to swell for 24 h in the electrolyte solution to ensure complete penetration. For these test electrodes, only 10% of active material was used, because this proved to be the optimum to confirm the function and the stability of the electrode. A ratio of three to seven of VGCF to graphite was chosen due to better processability. The polyacetylene backbone was specifically chosen for the use as a battery material because of its conjugated structure. The idea was to decrease the amount of conductive additive by introducing a conductive polymer. However, ultimately this advantage is overshadowed by unwanted disadvantages like side reactions of the backbone during oxidation.

Charge–discharge experiments were performed at 2C (1C equals charging/discharging in 1 h, 2C equals charging/discharging in 1/2 h, etc.) with both tested materials and showed capacities in the range of 30–35 mA h g^{-1} (Figure 3). This value corresponds to 60% theoretical capacity, which is in good accordance to

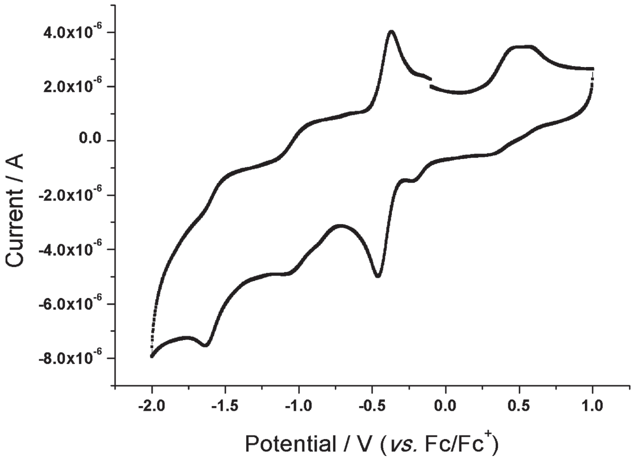


Figure 2. Cyclic voltammogramm of **4** (0.1 V s^{-1}; 0.1 M Bu_4NPF_6 in DMF).

the radical content of about 70%. The cycle stability in the aqueous electrolyte system was studied in 40 cycles; the capacity dropped to 50% or 40%, respectively (Table 2). Capacity loss may have occurred through washing-out of the material. To address this problem, more binder could be added to the electrode paste, but this also leads to losses in conductivity, and the possibility of the whole electrode mixture detaching as a film from the electrode or problems with processing, due to the mixture becoming too rubber like. Another reason for the lowering of the capacities can also be the presence of trace oxygen, which can oxidize the reduced galvinol species and thus reduce the capacity. Nevertheless, these measurements indicate that polyphenylacetylene-based galvinoxyles can be used in aqueous electrolytes for ORBs.

3.3. All-Organic Radical Battery

Lastly, an all-organic radical battery consisting of (*p*-ethynylphenyl)hydrogalvinoxyl and PTMA was studied. This cell was tested with an aqueous 0.1 M NaCl as electrolyte. This electrolyte was used because of its neutral pH value, the suitable potential window and the environment friendliness. As reported in the literature, PTMA works best under neutral or even slightly acidic[23] and, in contrast, galvinoxyls best under basic conditions.[12] The constructed battery system showed the expected charge–discharge behavior with a capacity of 38 mA h g^{-1}, which corresponds to 70% of its theoretical

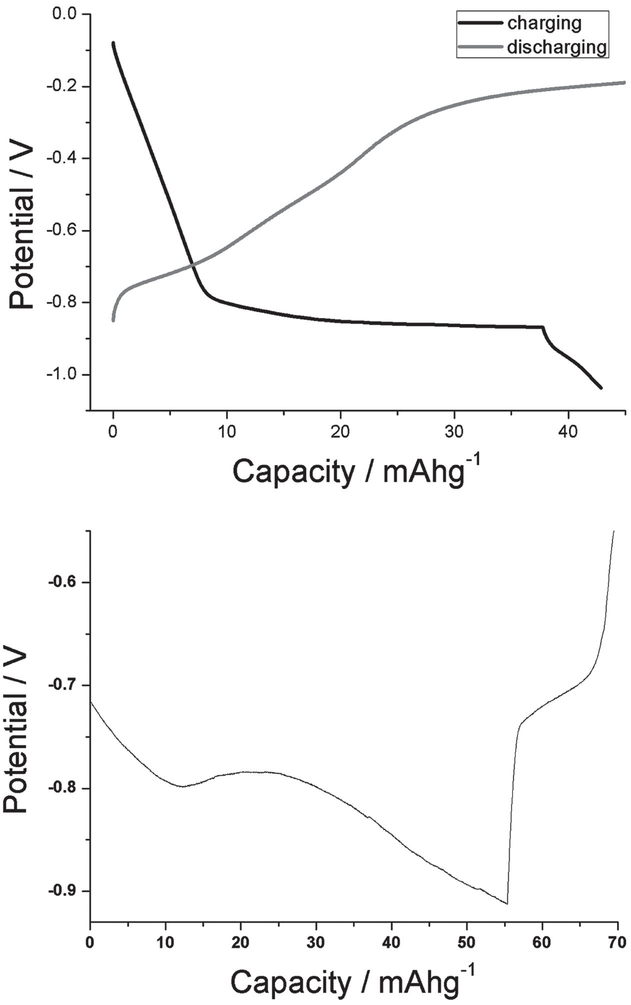


Figure 3. Charge and discharge experiment of **4** (top), **5** (bottom).

Table 2. Charge–discharge capacities of polymer half-cells and a full-organic radical battery.

Polymer/cycle	Charge capacity [mA h g^{-1}]	Percentage of theoretical charge capacity [%]	Discharge capacity [mA h g^{-1}]	Percentage of theoretical discharge capacity [%]	Efficiency [%]
4 – cycle 1	32	60	25	46	77
4 – cycle 40	26	48	21	39	81
5 – cycle 1	30	56	17	31	57
5 – cycle 40	22	41	14	26	63
All-organic battery	38	69	27	50	72

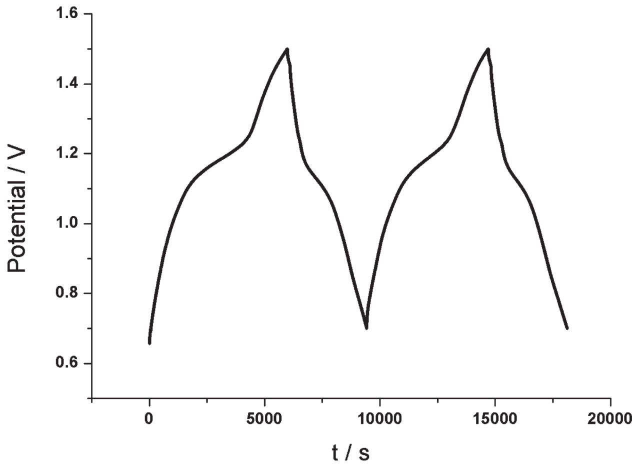


Figure 4. Charge–discharge cycles of a battery made from PTMA and poly-**4**.

capacity (Figure 4), but again with a lower discharge than charge capacity of 27 mA h g^{-1} (Table 2). This may be a result of the non-optimal electrolyte and the non-stabilized galvinolate anion, the influence of the polyacetylene as described above or self-discharge phenomena.[24] To enhance the performance of this cell, it is necessary to find conditions in which both the galvinolate anion and the TEMPO are stabilized. This will be the target of further studies.

4. Conclusion

Two acetylene-bearing galvinol monomers were synthesized, polymerized using a rhodium catalyst, oxidized, and evaluated for their use as anode material for ORBs. With the development of new poly(acetylene)s with stable radicals to replace metals completely and the use of an aqueous electrolyte, ORBs show their potential as an environmentally benign energy-storage system. Furthermore, since potentially no metals are needed for this type of battery and the possibility of producing organic compounds from renewable resources, ORBs are not limited by the dwindling amounts of expensive lithium and other metals commonly used in batteries. The synthesized radical polymers showed reversible redox reactions over dozens of cycles and are stable under ambient conditions for months. The use of an aqueous electrolyte gives the possibility of using these cells in biological environments, for example, in biochips. The fabricated all-organic radical battery represents a first step to the use of synthetic polymers in future devices, also using inkjet printing as a processing technique.[25]

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[1] K. Oyaizu, H. Nishide, *Adv. Mater.* **2009**, *21*, 2339.
[2] S. Komaba, T. Tanaka, T. Ozeki, T. Taki, H. Watanabe, H. Tachikawa, *J. Power Sources* **2010**, *195*, 6212.
[3] K. Koshika, N. Sano, K. Oyaizu, H. Nishide, *Chem. Commun.* **2009**, *45*, 836.
[4] K. Koshika, N. Chikushi, N. Sano, K. Oyaizu, H. Nishide, *Green Chem.* **2010**, *12*, 1573.
[5] H. Nishide, T. Suga, *Electrochem. Soc.* **2005**, *14*, 32.
[6] K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, J. Iriyama, M. Suguro, E. Hasegawa, *Chem. Phys. Lett.* **2002**, *359*, 351.
[7] M. Suguro, A. Mori, S. Iwasa, K. Nakahara, K. Nakano, *Macromol. Chem. Phys.* **2009**, *210*, 1402.
[8] R. G. Hicks, *Stable Radicals, Fundamentals and Applied Aspects of Odd-Electron Compounds*, John Wiley & Sons, Chichester, UK **2010**.
[9] Y. Yonekuta, K. Susuki, K. Oyaizu, K. Honda, *J. Am. Soc. Chem.* **2007**, *129*, 14128.
[10] T. Suga, H. Oshiro, S. Sugita, K. Oyaizu, H. Nishide, *Adv. Mater.* **2009**, *21*, 1627.
[11] N. Ouchi, M. Sato (Murata Manufacturing Co. Ltd.), *US 0195297 A1*, **2011**.
[12] T. Suga, S. Sugita, H. Ohshiro, K. Oyaizu, H. Nishide, *Adv. Mater.* **2011**, *23*, 751.
[13] J. Lee, E. Lee, S. Kim, G. S. Bang, D. A. Shultz, R. D. Schmidt, M. D. E. Forbes, H. Lee, *Angew. Chem Int. Ed.* **2011**, *50*, 4414.
[14] T. Kaneko, H. Tatsumi, T. Aoki, E. Oikawa, H. Yoshiki, N. Yoshioka, E. Tsuchida, H. Nishide, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 189.
[15] P. Wautelet, P. Turek, J. Le Moigne, *Synthesis* **2002**, *9*, 1286.
[16] M. Miyasaka, T. Yamazaki, H. Nishide, *Polym. J.* **2001**, *33*, 849.
[17] T. Kaneko, H. Abe, T. Namikoshi, E. Marwanta, M. Teraguchi, T. Aoki, *Synth. Met.* **2009**, *159*, 864.
[18] H. Nishide, K. Koshika, K. Oyaizu, *Pure Appl. Chem.* **2009**, *81*, 1961.
[19] R. M. Lucente-Schultz, V. C. Moore, A. D. Leonard, B. K. Price, D. V. Kosynkin, M. Lu, R. Partha, J. L. Conyers, J. M. Tour, *J. Am. Chem. Soc.* **2009**, *131*, 3934.
[20] T. Janoschka, A. Teichler, A. Krieg, M. D. Hager, U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 1394.
[21] R. R. Schrock, J. A. Osborn, *Inorg. Chem.* **1970**, *9*, 2339.
[22] F. Benière, D. Boils, H. Canepa, J. Franco, A. Le Corre, J. P. Louboutin, *J. Electrochem. Soc.* **1985**, *132*, 2100.
[23] T. Janoschka, M. D. Hager, U. S. Schubert, *Adv. Mater.* **2012**, *24*, 6397.
[24] K. Nakahara, J. Iriyama, S. Iwasa, M. Suguro, M. Satoh, E. J. Cairns, *J. Power Sources* **2007**, *165*, 398.
[25] T. Janoschka, A. Teichler, B. Häupler, T. Jähnert, M. D. Hager, U. S. Schubert, *Adv. Energy Mater.* **2013**, *3*, 1025.

Publication P2

P2) “Polymers based on stable phenoxyl radicals for the use in organic radical batteries”

T. Jähnert, B. Häupler, T. Janoschka, M. D. Hager, U. S. Schubert, *Macromol. Rapid Commun.* **2014***, 35,* 882−887.

Polymers Based on Stable Phenoxyl Radicals for the Use in Organic Radical Batteries

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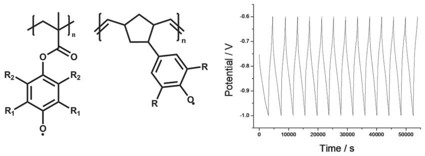
Polymers with pendant phenoxyl radicals are synthesized and the electrochemical properties are investigated in detail. The monomers are polymerized using ring-opening metathesis polymerization (ROMP) or free-radical polymerization methods. The monomers and polymers, respectively, are oxidized to the radical either before or after the polymerization. These phenoxyl radicals containing polymers reveal a reversible redox behavior at a potential of –0.6 V (vs Ag/AgCl). Such materials can be used as anode-active material in organic radical batteries (ORBs).



1. Introduction

Since the first report of an organic radical battery (ORB) based on poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA) by Nakahara et al.[1] in 2002, the number of publications in this field has been steadily increasing, which can largely be attributed to the extensive research of Oyaizu and Nishide.[2] The strong interest in ORBs has led to the development of a wide range of new redox-active polymers such as nitronyl nitroxides and many different nitroxide variations.[2] One of the major advantages of ORBs over conventional secondary batteries is their fast charging and discharging behavior (minutes instead of hours).[3] This is coupled to an excellent cycle life of 2000 or more cycles[3] without substantial loss of capacity, environmental friendliness without the use of heavy metals, nonflammability, high thermal and chemical stability, and also their potentially low production costs.[4]

Many publications about ORBs focus on the study of cathode materials. Very often TEMPO-based polymers are employed with varying polymer backbones such as methacrylate, vinylether, norbornene, or siloxane.[3,5–8] Similar stable radicals based on nitroxides have also been studied for their use as battery material,[9,10] but with less attention than TEMPO.

The metals lithium (as well as lithium graphite) and zinc are widely used as anode materials. Only in few studies, organic anode materials, for instance, galvinoxyl-, nitronyl nitroxide-, or viologene-based polymers have been investigated as anode-active materials in order to fabricate an all-organic radical battery.[3,11,12]

Phenoxyl radicals have been studied as products of the metabolism of β_2-agonists salbutamol and fenoterol,[13] for their hydrogen-bonding capabilities,[14,15] and in metal complexes.[16,17] Additionally, these radicals were employed in poly(3-radical-substituted thiophene)s and poly(phenylene vinylene)s to study their magnetic and electrical properties.[18,19] A study investigating bond-dissociation energy of phenols shows the stability of phenoxyl radicals, if they possess substituents such as *tert*-butyl or methoxy in *ortho*- and *para*-positions.[20] In comparison to established anode materials like galvinoxyles,

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phenoxyl radical polymers have a lower redox potential and, because of their significantly lower molar mass, a higher theoretical capacity.[12]

We succeeded in the synthesis of new phenoxyl radical bearing norbornenes and methacrylates, respectively, as polymerizable groups and performed successfully their polymerization using ROMP or free-radical polymerization. The electrochemical properties of the resulting polymers were investigated under different conditions and the polymers were tested as anode materials for organic radical batteries (ORBs).

2. Results and Discussion

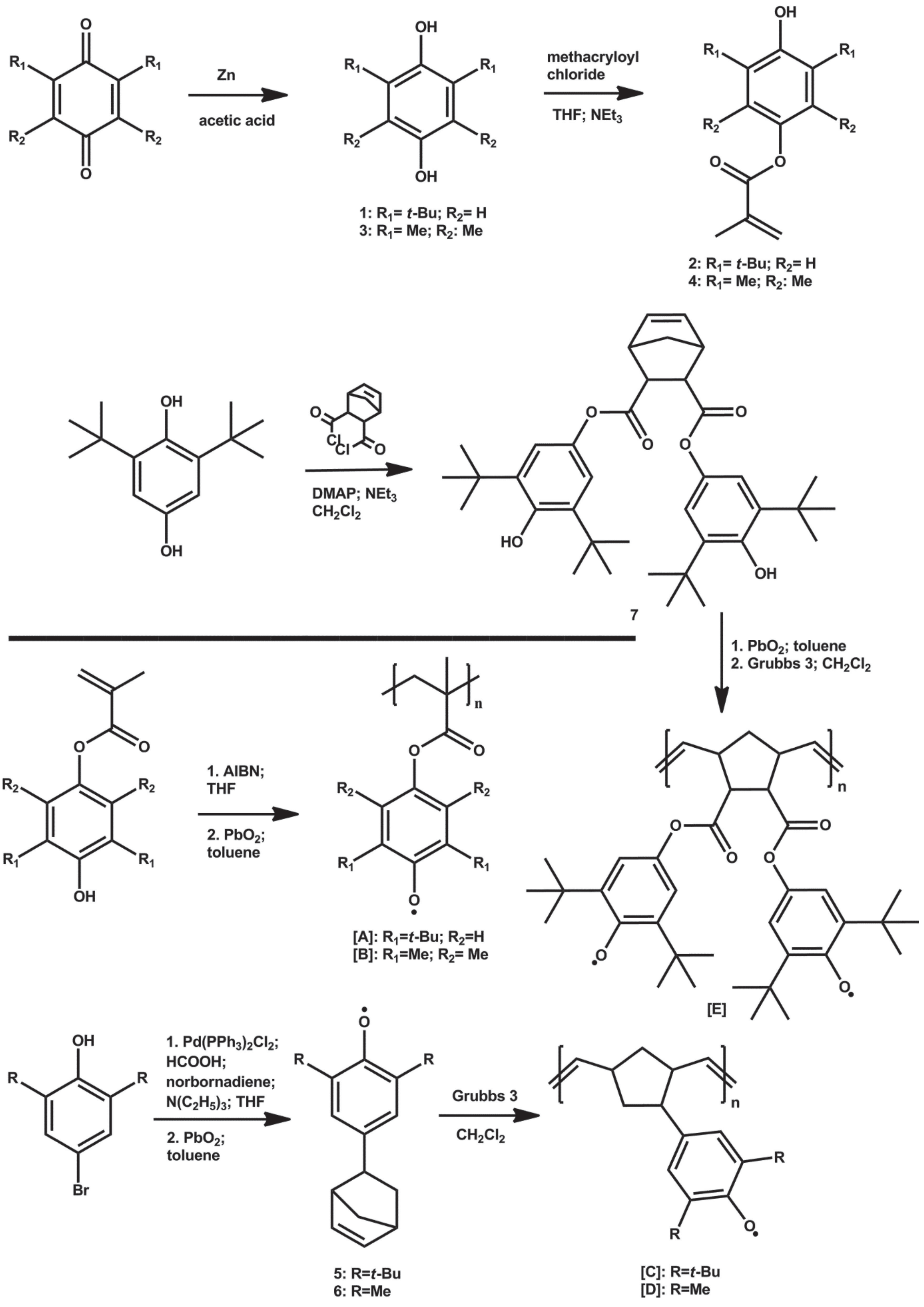
2.1. Synthesis and Characterization

The methacrylates **2** and **4** were synthesized in a straightforward way, starting from the commercially available 2,6-di-*tert*-butyl-1,4-benzoquinone and duroquinone. The quinones were reduced using zinc powder in glacial acetic acid to give their corresponding hydroquinones **1** and **3** in high yields (Scheme 1). Both hydroquinones were converted to the corresponding *p*-methacrylate phenols **2** and **4** by esterification with one equivalent methacryloyl chloride to avoid the formation of the double-substituted side product.

The polymerization of the monomers **2** and **4** was performed utilizing the free-radical polymerization technique with azobisisobutyronitrile (AIBN) as initiator (Scheme 1). A monomer ratio of 100:1 was chosen to obtain polymers with preferably high molar mass. Polymer [**A**] was obtained with a molar mass of M_n = 31 200 g mol^{-1} and a PDI value of 1.34 (SEC:PMMA calibration). In a similar manner, polymer [**B**] was obtained with a molar mass of M_n = 25 700 g mol^{-1} and a PDI value of 1.28 (SEC:PMMA calibration). Both polymers were still soluble in toluene and, therefore, could be oxidized with lead dioxide to form their stable radicals. After oxidation the molar masses measured via SEC increased with a rise of the PDI values, which occurs due to side reactions like cross-linking (as depicted in Table 1). Norbornene monomer **7** was synthesized via esterification of **1** with commercially available *trans*-5-norbornene-2,3-dicarbonyl chloride (Scheme 1). A slight excess of **1** was used to ensure a complete reaction to the double-substituted norbornene 7, which was obtained in 70% yield. The substituted norbornenes **5** and **6** were synthesized as a mixture of isomers both in good yields (Scheme 1) using 4-bromo-2,6-di-*tert*-butylphenol and 4-bromo-2,6-methylphenol as starting material via a reductive Heck reaction.[21] The norbornene monomers were oxidized utilizing lead dioxide in toluene prior to polymerization to ensure a high radical density of the polymer (Scheme 2). Grubbs 2nd- and 3rd-generation catalysts have been proven to tolerate a wide range of different functional groups such as carbazole[22] and succinimide[23] and also different stable organic radicals like nitronyl nitroxide.[24] The ability to polymerize stable organic radicals is, among others, one significant advantage of the ring-opening metathesis polymerization (ROMP) compared with classical radical polymerization techniques. For the polymerization, the monomers were dissolved in dichloromethane and the Grubbs 3rd-generation catalyst was added under nitrogen atmosphere. To obtain polymers that are insoluble in common organic electrolytes, a monomer to catalyst ratio of 100:1 was chosen for the polymerization. The obtained polymers [**C**] and [**D**] were insoluble in most common solvents. Polymer [**C**] could be dissolved in *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide and a SEC measurement in *N*,*N*-dimethylacetamide revealed a M_n of 455 000 g mol^{-1} and a PDI value of 2.31 for polymer [**C**]. Polymer [**E**] was obtained in a similar manner with a M_n of 41 600 g mol^{-1} and a very narrow molar mass distribution (PDI = 1.09). The higher PDI value for polymer [**C**] can be explained by the high reactivity of the used catalyst, which can lead to intermolecular reactions and a broader molar mass distribution.[25]

2.2. Electrochemistry

All soluble and radical-bearing compounds were examined using cyclic voltammetry to investigate their electrochemical behavior under different conditions. All oxidized monomers (Figure S1, Supporting Information) and polymers show a stable CV signal between –0.55 and –0.65 V (vs Ag/AgCl) depending on their substitution pattern. The oxidized polymers feature the same electrochemical behavior as their respective monomers, indicating that the polymer backbone has no influence on the redox chemistry of the radicals. Up to 100 cycles of every substance were measured without any degradation of the CV signal. The methacrylate-based phenoxyles of polymers [**A**] and [**B**] exhibit a reversible redox reaction at –0.55 V (vs Ag/AgCl), which is also present in polymers [**C**] and [**D**] with norbornene backbones (Figure 1). The influence of the backbones on the redox potential in these cases is negligible as is the influence of the methyl- and *tert*-butyl substituents. Only polymer [**E**] displays a slightly different redox potential of –0.6 V (vs Ag/AgCl) as seen in Figure 1. In comparison to the other compounds, polymer [**E**] is the only one with two redox-active units per repeating unit. Electrodes were prepared from radical polymers [**A**], [**C**], and [**E**] and subsequently investigated for their charge and discharge behavior. An electrode composition with only 10% active material was chosen for these tests, because of processability reasons. In attempts to construct electrodes



Scheme 1. Schematic representation of the synthesis of compounds **1**, **2**, **3**, **4**, and **7** (top). Schematic representation of the synthesis of polymers [**A**] and [**B**] using free-radical polymerization at 70 °C as well as synthesis of **5**, **6** by reductive Heck reaction and polymers [**C**], [**D**], and [**E**] by ring-opening metathesis polymerization (ROMP, bottom).

Table 1. Molar masses and polydispersity index values of the synthesized polymers.

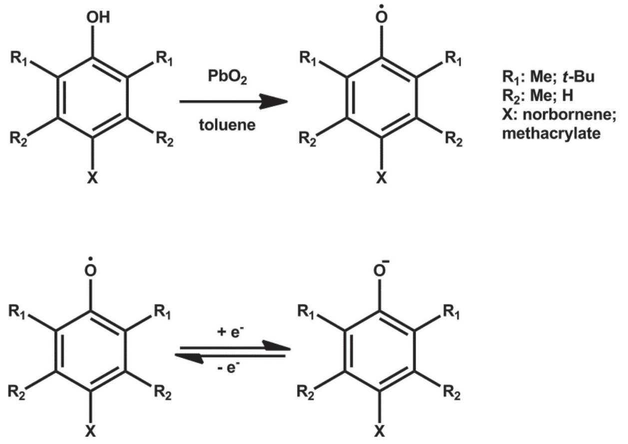
Polymer	Polymer backbone	M_n[a)] [g mol^{-1}]	M_w[a)] [g mol^{-1}]	PDI
[**A**]	Methacrylate	31 200	41 800	1.34
[**A**] oxidized	Methacrylate	23 700	72 600	3.06
[**B**]	Methacrylate	25 700	32 900	1.28
[**B**] oxidized	Methacrylate	23 400	66 900	2.86
[**C**]	Norbornene	455 000	1 050 000	2.31
[**D**]	Norbornene	Insoluble gel		
[**E**]	Norbornene	41 600	45 300	1.09

a)Determined by SEC (DMAc, PMMA calibration for methacrylic polymers, PS calibration for norbornene polymers).

with higher content of active material, it was discovered that the formed paste is then more difficult to apply to the graphite sheet substrate, because the paste became more and more rubber like. In the cases of the high molar mass polymers [**C**] and [**D**], this was even more predominant. After drying the electrodes, this would lead to inhomogeneous films on the substrate. As conductive additive, a mixture of graphite and vapor-grown carbon fibers (VGCF) was chosen. With their large volume, VGCF provides the basis for the electrode mixture, but would be too voluminous as only graphite source. Polyvinylidene fluoride was added as binder to improve the adhesion to the substrate surface.

After tests of several organic solvents, e.g., acetonitrile (Figure S2, Supporting Information) and propylene carbonate as electrolytes, a 0.1 M solution of sodium chloride and 0.1 M tetrabutylammonium hydroxide in water was identified as the best electrolyte. It was discovered that phenoxyl radicals like galvinoxyl radicals require a basic environment to function properly.[11] Polymer [**A**] was measured in the aforementioned basic electrolyte and exhibited 55% of its theoretical capacity for the first charging cycle with steadily decreasing values for additional cycles (Figure 1). If oxygen was present, the capacity decreased rapidly to about 7% of the theoretical capacity. Under oxygen-free conditions, charging capacities decrease over 40 cycles from 51 to 18 mAh g^{-1} (20% theoretical capacity). Discharging capacities can be calculated to roughly 50% of charging capacities. Experiments at higher currents (1 C and more) revealed a decreased capacity of the polymer to 20 mAh g^{-1} and less.

Charging and discharging experiments of electrodes fabricated from polymer [**C**] revealed a more stable behavior. Charging capacities held steady at 72 mAh g^{-1} for the first cycles, which is 80% of the polymers theoretical charge capacity. Over the measured 50 cycles, the



Scheme 2. Schematic representation of the oxidation of monomers/polymers (top) and reversible redox reaction of phenoxyl radicals (bottom) used as anode-active material in organic radical batteries.

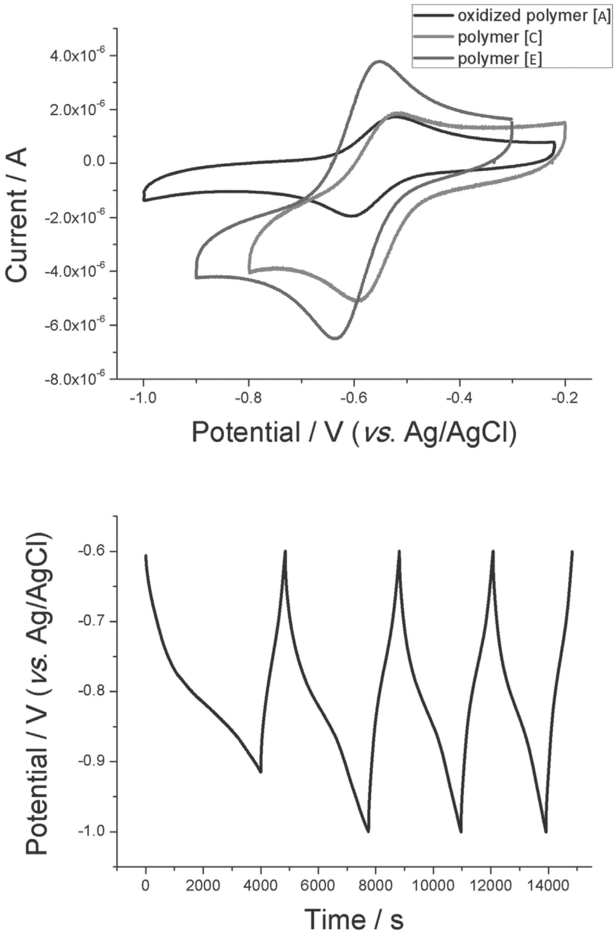


Figure 1. Cyclic voltammogram of the oxidized polymers [**A**], [**C**], and [**E**] (0.1 V s^{-1}; 0.1 M Bu$_4$NPF$_6$ in DMF) (top). Charge–discharge cycling of electrodes prepared from polymer [**A**] at 0.5 C using a solution of NaCl and tetrabutylammonium hydroxide in water (bottom).

charging capacity decreased by 10% to 64 mAh g^{-1}. Discharging capacities were measured to 44% of the initial charging capacities, which correspond to 40 mAh g^{-1}. After 50 cycles, discharge capacities remained unchanged (Figures S3 and S4, Supporting Information). The electrodes were charged and discharged at a rate of 1 C, to avoid losses in capacity, which were observed with higher capacities.

The behavior of polymer [**E**] differs from that of the other polymers. During the first cycles, the charging and discharging capacities rise to 75 and 60 mAh g^{-1}, respectively. The reason for this is the required full penetration of the electrode material with electrolyte. Afterward, the capacities stay at this level for the measured 100 cycles. No degradation could be observed. Even at higher currents (4 C) stable measurements without loss in capacity could be performed (Figures S5 and S6, Supporting Information). The compound maintained charge capacities of 82% and discharge capacities of 66% of its theoretical values, which translate to an efficiency of 80%.

These higher capacities may also be in regards to the higher radical concentration in the norbornene polymers. Electron paramagnetic resonance shows a radical concentration on average of 91% for polymers [**C**], [**D**], and [**E**] and 73% for polymers [**A**] and [**B**]. This demonstrates that the oxidation of monomers—**5**, **6,** and **7** were oxidized and then polymerized, while **2** and **4** were polymerized and then oxidized—is more effective than the oxidation of polymers. Experiments were also envisioned to fabricate an all-organic radical battery with a phenoxyl polymer as anode material and PTMA as cathode material. However, due to the basic electrolyte, which is required for the phenoxyl polymers, the use of PTMA is not possible. TEMPO-based radical polymers show irreversible redox reactions under basic conditions;[26] as a consequence, a different cathode material than the gold standard PTMA has to be used to fabricate all-organic ORBs with phenoxyl radical-containing polymers.

3. Conclusion

The existence of phenoxyl radicals has been known for decades, organic radical batteries (ORBs) are known since 2002, but the combination of both is presented for the first time in this contribution. Five different polymers based on phenoxyl radicals have been synthesized and characterized. These polymers were synthesized starting from the respective phenols or quinones, using methacrylate or norbornene as polymer backbone and possessing the stable phenoxyl radical in the side chain. Reversible redox reactions at relatively low potentials of –0.6 V (vs Ag/AgCl) could be observed. These redox potentials can possibly be adjusted through the introduction of substituents like nitrile or methoxy moieties, as can be seen with nitroxide radicals.[27] Half-cells were fabricated from the synthesized polymers and charge and discharge experiments were performed. These experiments revealed the *bis*-phenoxyl-substituted polymer [**E**] to possess high capacities and efficiency with no loss thereof after 100 cycles.

Since phenoxyl radicals have a lower molar mass than comparable anode materials like galvinoxyls, but feature also a reversible redox reaction at a lower potential, they can be used to fabricate electrodes for ORBs with higher capacities and cell potentials and could prove to be a valuable class of anodic materials for ORBs. The fabrication of the first all-organic radical battery based on phenoxyl radicals will be the target of further experiments.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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[1] K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, J. Iriyama, M. Suguro, E. Hasegawa, *Chem. Phys. Lett.* **2002**, 351.
[2] K. Oyaizu, H. Nishide, *Adv. Mater.* **2009**, *21*, 2339.
[3] K. Koshika, N. Chikushi, N. Sano, K. Oyaizu, H. Nishide, *Green Chem.* **2010**, *12*, 1573.
[4] Y. Dai, Y. Zhang, L. Gao, G. Xu, J. Xie, *J. Electrochem. Soc.* **2011**, A291.
[5] S. S. Iwasa, M. Suguro, N. Natori, K. Nakahara, J. Iriyama, M. Satoh, H. Nishide, *Electrochim. Acta* **2004**, *50*, 827.
[6] S. Komaba, T. Tanaka, T. Ozeki, T. Taki, H. Watanabe, H. Tachikawa, *J. Power Sources* **2010**, *195*, 6212.
[7] K. Koshika, N. Sano, K. Qyaizu, H. Nishide, *Chem. Commun.* **2009**, 836.
[8] M. Suguro, A. Mori, S. Iwasa, K. Nakahara, K. Nakano, *Macromol. Chem. Phys.* **2009**, *210*, 1402.
[9] K. Oyaizu, T. Suga, K. Yoshimura, H. Nishide, *Macromolecules* **2008**, *41*, 6646.
[10] K. Oyaizu, T. Kawamoto, T. Suga, H. Nishide, *Macromolecules* **2010**, *43*, 10382.
[11] T. Suga, S. Sugita, H. Ohshiro, K. Oyaizu, H. Nishide, *Adv. Mater.* **2011**, *23*, 751.
[12] T. Suga, H. Ohshiro, S. Sugita, K. Oyaizu, H. Nishide, *Adv. Mater.* **2009**, *21*, 1627.
[13] K. Reszka, D. W. McGraw, B. E. Britigan, *Chem. Res. Toxicol.* **2009**, *22*, 1137.

[14] M. Orio, O. Jarjayes, B. Baptiste, C. Philouze, C. Duboc, J.-L. Mathias, L. Benisvy, F. Thomas, *Chem. Eur. J.* **2012**, *18*, 5416.
[15] R. Wanke, L. Benisvy, M. L. Kuznetsov, M. F. C. G. da Silva, A. J. L. Pombeiro, *Chem. Eur. J.* **2011**, *17*, 11882.
[16] K. Butsch, A. Klein, S. Nitsche, K. Stirnat, J. R. Hawkett, E. J. L. McInnes, M. Bauer, *Dalton Trans.* **2012**, *41*, 11464.
[17] M. J. Zdilla, J. L. Dexheimer, M. M. Abu-Omar, *J. Am. Chem. Soc.* **2007**, *129*, 11505.
[18] M. Miyasaka, T. Yamazaki, E. Tsuchida, H. Nishide, *Polyhedron* **2001**, *20*, 1157.
[19] H. Nishide, M. Miyasaka, E. Tsuchida, *Angew. Chem Int. Ed.* **1998**, *37*, 2400.
[20] M. Lucarini, P. Pedrielli, G. F. Pedulli, *J. Org. Chem.* **1996**, *61*, 9259.
[21] A. M. Harned, H. S. He, P. H. Toy, D. L. Flynn, P. R. Hanson, *J. Am. Chem. Soc.* **2005**, *127*, 52.
[22] D. Liaw, C. Huang, E. Kang, *Polymer* **2006**, *47*, 3057.
[23] R. Bandari, J. Kuballa, M. R. Buchmeiser, *J. Sep. Sci.* **2013**, *36*, 1169.
[24] T. Sukegawa, A. Kai, K. Oyaizu, H. Nishide, *Macromolecules* **2013**, *46*, 1361.
[25] B. A. Buchholz, J. M. Zahn, M. Kenward, G. W. Slater, A. E. Barron, *Polymer* **2004**, *45*, 1223.
[26] K. Koshika, *Synthesis of Hydrophilic Radical Polymers and Their Application to an Organic Secondary Battery, Ph.D. Thesis*, Waseda University(Tokyo) 2009.
[27] T. Janoschka, M. D. Hager, U. S. Schubert, *Adv. Mater.* **2012**, *24*, 6397.

Publication P3

P3) “Polymers with *n*-type nitroxide side groups: Synthesis and electrochemical characterization”

T. Jähnert, T. Janoschka, M. D. Hager, U. S. Schubert, *Eur. Polym. J.* **2014**, *61*, 105–112.

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Polymers with n-type nitroxide side groups: Synthesis and electrochemical characterization

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ABSTRACT

This article describes the synthesis and electrochemical characterization of electroactive functionalized polymers with n-type nitroxides. Electron-poor phenyl nitroxide radicals with substituents like trifluoromethyl-, fluorine- or nitro-groups constitute the basic structural motif. The monomers were synthesized employing thio-“click” chemistry and polymerized by free radical polymerization or cationic polymerization techniques. The electrochemical properties of the resulting polymeric materials were investigated by cyclicvoltammetry. The monomers and polymers show reversible redox-reactions between −0.9 and −1.4 V (*vs.* Ag/AgCl) as well as a good stability over several cycles. These phenyl nitroxide radicals represent an interesting group of redoxactive polymers with highly negative redox-potentials, which makes them interesting candidates for organic radical batteries.

1. Introduction

Nitroxide-radicals are among the most well-known redox-active compounds [1]. Their respective redox-potentials vary depending on their structure – either embedded in a ring or in linear structures – and their substitution-pattern [2,3]. Nitroxide-radicals have been used for several decades as mediators for controlled radical polymerizations [4], as radical scavengers, ESR labels [5] and since 2002 as active material in organic radical batteries [6].

The first inorganic nitroxide was already discovered over 150 years ago [1] and the first organic nitroxide, porphyrexide, was introduced in 1901 by Piloty and Schwerin [7]. Today there are hundreds of stable nitroxide-radicals known and one of the most commonly used nitroxide is the 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO) radical [1–3,8–12]. Nitroxide-radicals are usually stable against water and air. As stable radicals they do not dimerize and are unaffected by many organic reactions, giving the opportunity to functionalize the radical-compound without affecting the radical site [1,4,13]. One aspect contributing to the stability of nitroxide-radicals is the suppression of side reactions by strategically introducing substituents in vulnerable positions. For phenyl nitroxides particularly the substituents in *ortho*- and *para*-position to the radical promote radical stability [14].

Typically, nitroxides are often embedded in rings, like the six-membered ring of the TEMPO-radical [8–12] or the five-membered ring in the PROXYL-radical [14]. These radicals are often used in organic radical batteries [2,3,5,6,8–12,15,16] and organic memory devices [17] because of their reversible redox-chemistry.

Apart from these nitroxides, other types can be found in acyclic structures usually with bulky substituents like *tert*-butyl or phenyl [1,18]. Some of these radicals have been very prominent as mediators for controlled radical polymerizations, like SG1 and TIPNO [19,20].

Nitroxides were often used as functional moieties in polymers. Common polymer-backbones functionalized

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with nitroxides are, e.g., methacrylate [6], acrylate [18], norbornene [12], vinylether [9], styrene [16] or acrylamide [8]. These materials, in particular polymers with TEMPO moieties, have been applied as redox-active material in organic radical batteries (ORBs). Their redox-potential was tuned by the introduction of substituents like trifluoromethyl-, cyanide- or methoxy-groups [2,3,16]. However, most of the described nitroxides are p-type materials, *i.e.* the radical can be oxidized. Nitroxides, which feature n-type behavior, *i.e.* the nitroxide can be reduced without subsequent decomposition, are scarce.

In this contribution the synthesis and characterization of nitroxide-radical-bearing small molecules as well as polymers with electron-withdrawing substituents is described. The electrochemical properties of the monomers and polymers, respectively, were analyzed *via* cyclicvoltammetry.

2. Experimental section

2.1. Materials

All organic reactions were performed under a nitrogen atmosphere. All used chemicals and solvents were purchased from Sigma–Aldrich, Acros Organics, Apollo Scientific as well as Alfa Aesar and were used without further purification unless otherwise specified. If not otherwise noted solvents were dried according to standard procedures. Dry THF and toluene were obtained from a Pure Solv MD-4-EN solvent purification system.

2.2. General procedures

Reactions were monitored by TLC (aluminum sheets coated with silica gel 60 F254 by Merck) and SEC (using a Shimadzu SCL-10A VP controller, a LC-10AD pump, a RID-10A refractive index detector, a SPD-10AD VP UV-detector and a PSS SDV pre/lin S column; temperature: 40 °C, eluent: chloroform:triethylamine:*iso*-propanol 94:4:2; flow rate: 1 mL/min, calibration: polystyrene).

SECs for the polymers were measured with a Shimadzu SCL-10A VP controller, a LC-10AD pump, a RID-10A refractive index detector, a SPD-10AD VP UV-detector and a PSS SDV pre/lin M (THF-N) column; temperature: 40 °C, eluent: THF; flow rate: 1 mL/min, calibration: polystyrene.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 250 (250 MHz) and a Bruker AC 300 (300 MHz) spectrometer at 298 K. Chemical shifts are reported in parts per million (ppm, δ scale) relative to the residual signal of the deuterated solvent.

Column chromatography was performed on silicagel 60 (Merck). Elemental analyses were carried out using a Vario ELIII – Elementar Euro and an EA – HekaTech.

ESI-Q-TOF-MS measurements were performed using a micrOTOF (Bruker Daltonics) mass spectrometer equipped with an automatic syringe pump which is supplied from KD Scientific for sample injection. The mass spectrometer was operating in the positive ion mode. The standard electrospray ion (ESI) source was used to generate the ions. Samples' concentrations ranging from 1 to 10 μg/mL were injected using a constant flow (3 μL/min) of sample solution. ESI solvents used in this study were dichloromethane, acetonitrile, chloroform or their mixtures. The ESI-Q-TOF-MS instrument was calibrated in the m/z range 50–3000 using an internal calibration standard (Tunemix solution) which is supplied from Agilent. Data were processed *via* Bruker Data Analysis software version 4.0. HR-MS calculations have been made by using this software. All solvents (dichloromethane, acetonitrile, and chloroform) used for the ESI-MS measurements were LC-MS grade solvents; they were purchased from Sigma Aldrich, and used as received.

Spin-concentrations were determined *via* electron spin resonance (ESR) on an X-band ESR-spectrometer (Bruker) using copper bromide as internal standard.

Electrochemical measurements were performed on a Princeton Applied Research Versastat potentiostat with a standard three-electrode configuration using a graphite-disk working electrode, a platinum-rod auxiliary electrode and an Ag/AgCl reference electrode. The experiments were carried out in deaired solvents containing tetra-*n*-butylammonium hexafluorophosphate salt (0.1 M). At the end of each measurement ferrocene was added as an internal standard.

2.3. Synthesis of N-(2,3-dimethylbut-3-en-2-yl)-N-(pentafluorophenyl)hydroxylamine (**1**)

To a solution of pentafluoroaniline (1.00 g, 5.46 mmol) in 15 mL dichloromethane a mixture of formic acid (4.50 mL, 120.22 mmol) and hydrogen peroxide (3.70 mL, 120.2 mmol) was added. The reaction mixture was heated under reflux for five hours. 20 mL water was added and the mixture was heated under reflux for another two hours. After cooling the organic phase was separated and washed twice with 20 mL water. After drying over Na_2SO_4 and removal of the solvent under reduced pressure pentafluoronitrosylbenzene was obtained as light blue solid. The nitrosyl-compound was used without further purification. A solution of the nitrosyl compound in 30 mL dichloromethane was stirred vigorously at 0 °C. Tetramethylethylene (3.25 mL, 27.33 mmol) was added dropwise and the resulting solution was stirred at 0 °C for one hour, subsequently washed with water and dried over Na_2SO_4. The remaining compounds were purified by column chromatography (Silica 60, dichloromethane|*n*-hexane 1:1) to give **1** as pale yellow crystals (1.13 g, 78%).

^{1}H NMR (250 MHz, $CDCl_3$, δ): 1.27 (CH_3, s, 6 H), 1.94 (CH_3, s, 3H), 4.98 (CH_2, s, 1H), 5.04 (CH_2, s, 1H), 5.24 (s, OH, 1H).

^{13}C NMR (60 MHz, $CDCl_3$, δ): 19.5 (CH_3, 3C), 22.4 (CH_3, 6C), 67.5 ($(CH_3)_2CN$, 1C), 112.9 (CH_2), 122.8 (C aromatic), 136.5 (3 CF aromatic), 142.7 (2 CF aromatic), 148.3 (CCH_2).

Anal. calcd for $C_{12}H_{12}F_5NO$: C 51.25; H 4.30; F 33.78; N 4.98; O 5.69; found: C 50.98; H 4.11; N 4.75.

HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{12}H_{12}F_5NO$, 304.2116; found, 304.2188.

*2.4. Synthesis of N,N′-((hexane-1,6-diylbis(sulfanediyl))bis(2,3,5,6-tetrafluoro-4,1-phenylene))bis(N-(2,3-dimethylbut-3-en-2-yl)hydroxylamine) (**2**)*

To a solution of **1** (1.00 g, 3.77 mmol) and triethylamine (3.93 mL, 28.31 mmol) in 20 mL DMF 1,6-hexanedithiol (0.29 mL, 1.89 mmol) was very slowly added dropwise. The reaction mixture was stirred at room temperature for 20 h. After subsequent extraction with diethyl ether and washing with 20 mL water the organic phase was dried over $MgSO_4$ and the solvent removed under reduced pressure. The remaining compounds were purified by column chromatography (Silica 60, toluene) to give **2** as pale yellow oil (0.94 g, 74%).

^1H NMR (300 MHz, $CDCl_3$, δ): 1.28 (CH_3, s, 6H), 1.42 (CH_2, q, J = 6.8 Hz, 4H), 1.59 (CH_2, q, J = 10.8 Hz, 4H), 1.95 (CH_3, s, 3H), 2.93 (CH_2, t, J = 6.8 Hz, 4H), 4.99 (CH_2, s, 1H), 5.05 (CH_2, s, 1H), 5.29 (s, OH, 2H).

^{13}C NMR (60 MHz, $CDCl_3$, δ): 19.5 (CH_3, 2C), 22.5 (CH_3, 4C), 27.9 (CH_2, 2C), 29.7 (CH_2, 2C), 38.8 (SCH_2, 2C), 67.8 ($(CH_3)_2C$, 2C), 111.0 (CH_2, 2C), 112.8 (SC aromatic, 2C), 122.9 (NC aromatic, 2C), 142.2 (CF aromatic, 4C), 146.1 (CF aromatic, 4C), 148.5 (CH_2C, 2C).

Anal. calcd for $C_{30}H_{36}F_8N_2O_2S_2$: C 53.56; H 5.39; F 22.59; N 4.16; O 4.76; S 9.53; found: C 53.63; H 5.74; N 3.81; S 9.65.

HRMS (ESI) *m*/*z*: $[M+NH_4]^+$ calcd. for $C_{30}H_{36}F_8N_2O_2S_2$, 690.7747; found, 690.7734.

*2.5. Synthesis of N-(tert-butyl)-2,3,5,6-tetrafluoro-4-vinylaniline (**3**)*

Pentafluorostyrene (3.00 mL, 21.78 mmol), *tert*-butylamine (4.60 mL, 43.60 mmol) and potassium carbonate (3.00 g, 21.82 mmol) were suspended in 30 mL DMSO and stirred at 40 °C for five hours. This suspension was poured into ice water and subsequently extracted with 50 mL dichloromethane. After washing the combined organic phases three times with 50 mL water each, it was dried over Na_2SO_4 and the solvent and remaining *tert*-butylamine was removed under reduced pressure. **3** was obtained as colorless oil (3.81 g, 71%).

^1H NMR (300 MHz, $CDCl_3$, δ) 1.30 (CH_3, s, 9 H), 3.15 (s, NH, 1H), 5.58 (CH_2, d, J = 6.1 Hz, 1H), 5.72 (CH_2, d, J = 6.1 Hz, 1H), 6.64 (CH_2, q, J = 12.54 Hz, 1H).

^{13}C NMR (60 MHz, $CDCl_3$, δ): 28.8 (CH_3, 3C), 60.5 (CNH), 103.1 (CHC aromatic, 1C), 112.8 (CH_2), 120.7 (NHC aromatic), 136.0 ($CHCH_2$), 141.9 (2C aromatic), 142.5 (2C aromatic).

Anal. calcd for $C_{12}H_{13}F_4N$: C 58.30; H 5.30; F 30.74; N 5.67; found: C 58.48; H 5.43; N 5.89.

HRMS (ESI) *m*/*z*: $[M+Na]^+$ calcd. for $C_{12}H_{13}F_4N$, 270.2217; found, 270.2242.

*2.6. Synthesis of N-(2-(trifluoromethyl)phenyl)-methacrylamide (**4**)*

To a solution of 2-trifluoromethyl aniline (5.00 g, 31.00 mmol) and triethylamine (5.00 mL, 36.11 mmol) in 50 mL dichloromethane methacryloylchloride (6.14 mL, 62.39 mmol) was added under nitrogen at 0 °C. This solution was stirred for one hour at 0 °C, at room temperature for another twelve hours and subsequently poured into water. After extraction with 50 mL dichloromethane and drying over $MgSO_4$ the solvent was removed under reduced pressure. The crude product was purified by column chromatography (Silica 60, dichloromethane) to give **4** as white solid (4.52 g, 63%).

^1H NMR (300 MHz, $CDCl_3$, δ): 2.09 (CH_3, s, 3 H), 5.54 (CH_2, s, 1H), 5.88 (CH_2, s, 1 H), 7.24 (t, J = 7.8 Hz, 1H), 7.60 (m, 2H), 7.94 (NH, s, 1H), 8.36 (d, J = 4.77 Hz, 1H).

^{13}C NMR (60 MHz, $CDCl_3$, δ): 17.92 (CH_3, 1C), 117.2 (C aromatic), 118.6 (CH_2), 120.4 (CF_3C aromatic), 123.7 (C aromatic), 125.5 (CF_3), 125.8 (C aromatic), 132.4 (HNC aromatic), 134.9 (C aromatic), 139.7 (CCH_2), 165.6 ($C{=}O$).

Anal. calcd for $C_{11}H_{10}F_3NO$: C 57.64; H 4.40; F 24.87; N 6.11; O 6.98; found: C 57.96; H 4.49; N 6.03.

HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd. for $C_{11}H_{10}F_3NO$, 230.2063; found, 230.2068.

*2.7. Synthesis of N-(4-nitrophenyl)methacrylamide (**5**)*

To a solution of 4-nitro aniline (4.28 g, 31.11 mmol) and triethylamine (5.00 mL, 36.12 mmol) in 50 mL dichloromethane methacryloylchloride (6.11 mL, 62.40 mmol) was added under nitrogen at 0 °C. This solution was stirred one hour at 0 °C, at room temperature for another twelve hours and subsequently poured into water. After extraction with 50 mL dichloromethane and drying over $MgSO_4$ the solvent was removed at reduced pressure. The crude product was purified by column chromatography (Silica 60, dichloromethane) to give **5** as yellow solid (2.83 g, 65%).

^1H NMR (300 MHz, $CDCl_3$, δ): 2.08 (CH_3, s, 3H), 5.57 (CH_2, s, 1H), 5.86 (CH_2, s, 1H), 7.77 (d, J = 4.9 Hz, 2H), 7.91 (NH, s, 1H), 8.22 (d, J = 4.7 Hz, 2H).

^{13}C NMR (60 MHz, $CDCl_3$, δ): 18.6 (CH_3), 119.3 (CH_2), 121.1 (2C aromatic), 125.0 (2C aromatic), 140.3 (CCH_2), 143.5 (NO_2C aromatic), 143.7 (HNC aromatic), 166.7 ($C{=}O$).

Anal. calcd for $C_{10}H_{10}N_2O_3$: C 58.25; H 4.89; N 13.59; O 23.28; found: C 58.23; H 5.06, N 13.61.

HRMS (ESI) *m*/*z*: $[M+Na]^+$ calcd. for $C_{10}H_{10}N_2O_3$, 207.2059; found, 207.2075.

*2.8. Synthesis of N-(2,3-dimethylbut-3-en-2-yl)-N-(2-(trifluoromethyl)phenyl)hydroxylamine (**6**)*

To a mixture of 150 mL dichloromethane, formic acid (50.00 mL, 1.34 mol) and hydrogen peroxide (40.00 mL, 1.30 mol) 2-trifluoromethyl aniline (10.00 mL, 80.40 mmol) was added dropwise. The reaction mixture was heated under reflux for five hours. After cooling the organic phase was separated and washed three times with 150 mL water. After drying over Na_2SO_4 and removal of the solvent under reduced pressure 2-trifluoromethyl nitrosylbenzene was obtained as light blue solid. Without further purification the nitrosyl-compound was dissolved in 100 mL dichloromethane and tetramethylethylene (17.80 mL, 149.93 mmol) was added dropwise at 0 °C under vigorous stirring. This solution was stirred at 0 °C for one hour, subsequently washed with water and dried over Na_2SO_4. The remaining compounds were purified by column chromatography (Silica 60, dichloromethane|*n*-hexane 1:2) to give **1** as white solid (12.61 g, 60%).

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.27 (CH_3, s, 6H), 2.00 (CH_3, s, 3H), 5.1 (OH, s, 1H), 6.25 (CH_2, s, 1H), 6.28 (CH_2, s, 1H), 7.49 (d, *J* = 4.2 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.83 (t, *J* = 7.5 Hz, 1H), 8.03 (d, *J* = 4.5 Hz, 1H).

^{13}C NMR (60 MHz, $CDCl_3$, δ): 19.0 (CH_3), 22.6 (2 CH_3), 80.3 ($(CH_3)_2C$), 113.3 (CH_2), 122.3 (C aromatic), 124.9 (C aromatic), 126.7 (CF_3), 128.4 (C aromatic), 130.7 (C aromatic), 132.4 (C aromatic), 141.4 (NC aromatic), 147.0 (CH_2).

Anal. calcd for $C_{13}H_{16}F_3NO$: C 60.22; H 6.22; F 21.98; N 5.40; O 6.17; found: C 60.57; H 6.08; N 5.68.

HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd. for $C_{13}H_{16}F_3NO$, 260.2754; found, 260.2742.

2.9. Synthesis of N-(perfluorophenyl)methacrylamide (7)

To a solution of pentafluoroaniline (4.00 g, 21.90 mmol) and triethylamine (4.20 mL, 30.30 mmol) in 30 mL dry dichloromethane methacryloylchloride (2.93 mL, 29.19 mmol) was added under nitrogen at 0 °C. This solution was stirred for one hour at 0 °C, at room temperature for another four hours and subsequently poured into water. After extraction with 50 mL dichloromethane and drying over $MgSO_4$ the solvent was removed at reduced pressure. The crude product was purified by column chromatography (Silica 60, ethyl acetate|*n*-hexane 1:10) to give **7** as colorless oil (3.18 g, 58%).

^{1}H NMR (300 MHz, $CDCl_3$, δ): 2.07 (CH_3, s, 3H), 5.93 (CH_2, s, 1H), 6.23 (CH_2, s, 1H), 7.42 (OH, s, 1H).

^{13}C NMR (60 MHz, $CDCl_3$, δ): 18.8 (CH_3), 106.0 (HNC_{ar}), 122.3(CH_2), 129.0 (CF aromatic), 135.5 (2CF aromatic), 142.3 (CCH_2), 145.1 (2CF aromatic), 172.4 (C=O).

Anal. calcd for $C_{10}H_6F_5NO$: C 47.82; H 2.41; F 37.82; N 5.58; O 6.37; found: C 47.46; H 2.48; N 5.56.

HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd. for $C_{10}H_6F_5NO$, 252.1607; found, 215.1603.

2.10. General procedure for the polymerization: Free-radical polymerization

Methacrylic and styrene-based monomers were polymerized as follows: A solution of the monomer and AIBN (2 mol%) in THF (0.5 M) were purged in a microwave vial with nitrogen for 45 min. Styrene-monomers were polymerized at 70 °C for 10 h, while the methacrylamide-monomers were polymerized for 48 h. The reaction mixture was allowed to cool to room temperature and subsequently precipitated from hexane.

2.11. General procedure for the polymerization: Cationic polymerization

Isobutylene-monomers were polymerized using cationic polymerization techniques. The monomer was dissolved in dichloromethane (0.2 M) with 2,6-di-*tert*-butylpyridine (3 mol%) and the reaction mixture was cooled to −78 °C under nitrogen atmosphere. 2-Methyl-2-phenyloxirane (5 mol%) and titanium tetrachloride (3.5 mol%) were added dropwise and the reaction was stirred at −78 °C for three hours. The polymerization was quenched by adding methanol into the solution. After warming to room temperature the polymer was precipitated from hexane.

2.12. General procedure for the oxidation of monomers and polymers

Oxidation of the monomers and polymers was carried out as follows: A solution of the monomer/polymer in toluene (0.5 M) was purged with nitrogen for 30 min. PbO_2 (excess) was added and this suspension was stirred for two hours. After filtration and subsequent evaporation of the solvent under reduced pressure, the oxidized monomer/polymer was obtained.

3. Results and discussion

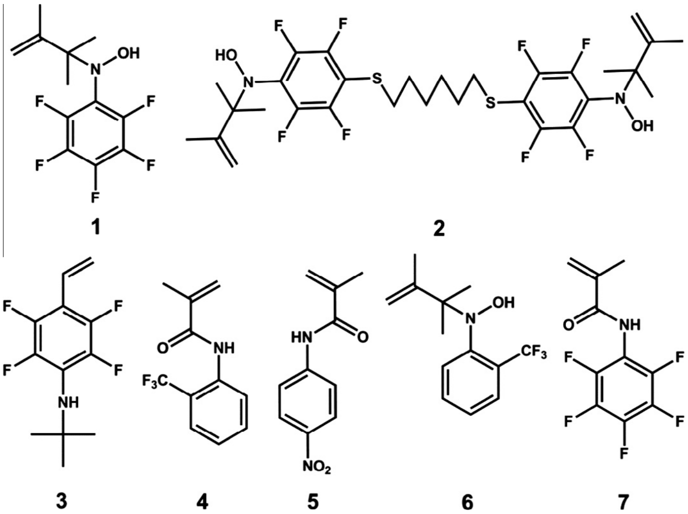
3.1. Synthesis and characterization

The synthesis of *N*-(2,3-dimethylbut-3-en-2-yl)-*N*-(pentafluorophenyl)hydroxylamine **1** can be divided into two steps. In the first step pentafluoroaniline was treated with formic acid and hydrogen peroxide to yield pentafluoro nitrosylbenzene. During this reaction a color-change can be observed in the organic phase of the two-phase reaction. This change from colorless to a deep blue indicates the formation of the nitrosyl-compound. This pentafluoro nitrosylbenzene was isolated as an almost colorless solid in form of its dimer. Subsequently, it was reacted with tetramethylethylene to form *N*-(2,3-dimethylbut-3-en-2-yl)-*N*-(pentafluorophenyl)hydroxylamine **1** through an ene-reaction. During the addition of the alkene, a distinct color-change could be observed again. The characteristic blue color of the nitrosyl changed very fast to a light yellow color and the desired compound **1** could be obtained in a yield of almost 80% (Scheme 1).

Following the synthesis of **1**, two of these compounds were coupled to form **2** *via* a thio-“click” reaction. To the pentafluorinated compound **1** 1,6-hexanedithiol was added very slowly to ensure a full reaction of both thiol-groups with the *para*-fluorines of **1**. During this reaction HF is produced, which was neutralized by the addition of triethylamine in the formation of triethylamine hydrofluoride. Compound **2** was obtained with 74% yield (Scheme 1).

A similar reaction was performed to prepare *N*-(*tert*-butyl)-2,3,5,6-tetrafluoro-4-vinylaniline **3**. Starting from pentafluorostyrene *tert*-butylamine was introduced at the *para*-position. *tert*-Butylamine was used in excess to substitute the *para*-fluorine atom and also to bind the emerging hydrogenfluoride. After the removal of the sodium carbonate, which was used as base, and distillation compound **3** was obtained with approximately 70% yield.

N-(2-(Trifluoromethyl)phenyl)methacrylamide **4** and *N*-(4-nitrophenyl)methacrylamide **5** were synthesized starting from their respective anilines by esterification with methacryloyl chloride under inert conditions. A double excess of methacryloyl chloride was used to ensure a higher yield for the reactions. When methacryloyl chloride



Scheme 1. Schematic representation of the synthesized monomers **1** to **7**.

was used in a stoichiometric amount and in slight excess, respectively, only yields of 30% or less were achieved. With 2 eq. methacryloyl chloride yields between 60% and 70% could be obtained.

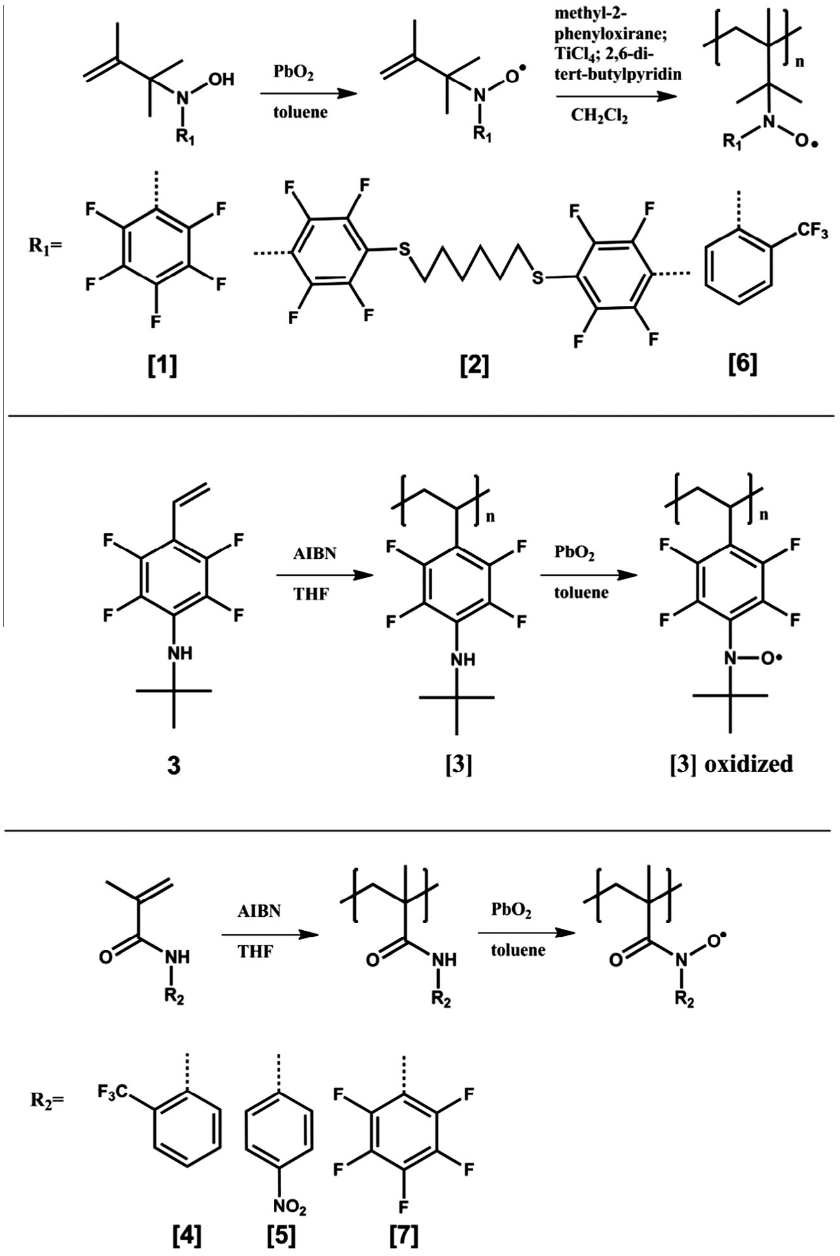
Similar to the synthesis of *N*-(2,3-dimethylbut-3-en-2-yl)-*N*-(pentafluorophenyl) hydroxylamine **1** *N*-(2,3-dimethylbut-3-en-2-yl)-*N*-(2-(trifluoromethyl)phenyl)hydroxylamine **6** was synthesized by adding formic acid and hydrogen peroxide to the solution of an aniline, in this case 2-trifluoromethyl aniline. 2-Trifluoromethyl nitrosylbenzene could be isolated as light blue solid, which was subsequently reacted with tetramethylethylene. The blue color of the nitrosyl-compound disappeared during the addition of the alkene and *N*-(2,3-dimethylbut-3-en-2-yl)-*N*-(2-(trifluoromethyl)phenyl)hydroxylamine **6** could be obtained after purification with a yield of 60% (Scheme 1).

Methacrylamide **7** was synthesized by reaction of pentafluoroaniline with methacryloyl chloride under inert conditions and addition of triethylamine as base. With only a slight excess of the acid chloride used *N*-(perfluorophenyl)methacrylamide **7** could be obtained in 58% yield.

The obtained monomers can be divided into three categories according to their polymerizable group: Styrene-derivative **3**, methacrylamides **4**, **5** and **7** and the *iso*-butylene-derivatives **1**, **2** and **6**. According to this differentiation the polymerization techniques had to be adapted. **3** was polymerized *via* a free-radical polymerization with AIBN at 70 °C for 10 h. The methacrylamide-derivatives were also polymerized *via* free-radical polymerization with AIBN as initiator, but the reaction times had to be extended to 48 hours to obtain higher conversion (Scheme 2). Molar masses of 16,800 g/mol (M_n) could be achieved for polymer [3] with a polydispersity index (PDI value) of 1.16 (Table 1). After oxidation the molar mass of the polymer increased slightly accompanied with an increase of the PDI value to 1.67 due to side-reactions caused by the formed radicals [21,22]. Methacrylamide polymer [4] was obtained with a molar mass of 9.700 g/mol (M_n) and a PDI value of 1.65. After oxidation of the polymer both values increased (M_n = 13,200 g/mol and PDI = 1.98). The polymerization of *N*-(4-nitrophenyl)methacrylamide **5** yielded polymer [5] with a molar mass of 8200 g/mol (M_n) and a very narrow PDI value of 1.05. This polymerization showed lower conversions (40%) than the other free-radical polymerization approaches. After oxidation PDI values of the polymer increased to 1.24, but its molar mass, obtained by SEC, decreased to 6500 g/mol. This may be due to the different hydrodynamic volume of the oxidized polymer compared to its predecessor or side-reactions caused by the radical [21]. Polymer [7] again revealed the expected behavior. The molar mass (M_n) of the polymer rises from 20,000 g/mol to 20,900 g/mol after oxidation, while the PDI values increase from 1.12 to 1.43 after oxidation (Table 1).

The *iso*-butylene monomers **1**, **2** and **6** could be polymerized *via* cationic polymerization. The polymerizations were performed using 2-methyl-2-phenyloxirane as initiator, titanium tetrachloride as co-initiator and 2,6-di-*tert*-butylpyridine as a proton trap. The initiator and co-initiator were added at −78 °C under a nitrogen-atmosphere to a solution of the monomer and 2,6-di-*tert*-butylpyridine in dichloromethane. After stirring for three hours under cooling the polymerizations were quenched with methanol and precipitated. To avoid a reaction with $TiCl_4$, the monomers were oxidized before the polymerization. This oxidation-step also ensures higher radical-concentrations in the polymers, because later oxidation of the polymer would be less efficient, due to the bulky polymer coils blocking the oxidation positions.

Polymer [1] was obtained with a molar mass (M_n) of 9200 g/mol and a PDI value of 1.22 (Table 1). Polymer [2] was insoluble after polymerization due to the bifunctional monomer **2**, which results in crosslinking during the polymerization. In the case of polymer [6] molar masses (M_n) of 11,400 g/mol were achieved, with a PDI value of 1.28. All polymers (except [2]) were soluble in standard organic solvents (*e.g.*, CH_2Cl_2, $CHCl_3$, THF, DMF, DMAc). Polymers [1] to [4] and [6] to [7] were colorless to a slight yellow



Scheme 2. Schematic representation of polymerization of monomers **1** to **7** (top: cationic polymerization of monomers **1**, **2** and **6**; middle: free-radical polymerization of monomer **3**; bottom: free-radical polymerization of monomers **4**, **5** and **7**).

color and polymer [5] possessed a deep yellow, almost orange color. The oxidized forms of polymers [3], [4] and [7] all showed a slightly orange color.

3.2. Electrochemistry

All soluble and redox-active compounds were characterized by cyclic voltammetry to investigate their electrochemical behavior under different conditions. The oxidized forms of methacrylamide polymers [4] and [5] showed redox-reactions at −1.66 V and −1.78 V (*vs.* Fc/Fc$^+$), respectively (Table 1; Fig. 1). An additional redox-signal can be observed for oxidized polymer [5] at −1.45 V, which is an irreversible reduction to precede the following reduction of the resulting polymer (Fig. 1). Polymer [6] is, apart from the polymerizable side-group, identical to oxidized polymer [4] and also shows a similar redox behavior. Polymers [1] and [2] both show a redox reaction at −1.31 V (*vs.* Fc/Fc$^+$) that is stable over several cycles (Fig. 1). Because of polymer [2]́s insolubility it had to be measured on a graphite electrode. For this purpose polymer [2] (10 mg), graphite (56 mg) and vapor grown carbon fibers (VGCF) (24 mg) as conductive additives and poly(vinylidenefluoride) (PVDF) (10 mg) as binder were

Table 1
Molar masses and polydispersity index values for polymers: (a) Determined by SEC (dimethylacetamide, PS-calibration); (b) determined by SEC (dimethylacetamide, PMMA-calibration) as well as redox potentials and theoretical capacities.

Polymer	Catalyst/initiator	M_n [g/mol]	M_w [g/mol]	PDI	Redox-potential [V *vs.* Fc/Fc$^+$]	Theoretical capacity [mAh$*$g^{-1}]
[1]	Methyl-2-phenyloxirane, $TiCl_4$	9200$^{(a)}$	11,200$^{(a)}$	1.22	−1.31	95
[2]	Methyl-2-phenyloxirane, $TiCl_4$	insoluble			−1.31	80
[3]	AIBN	16,800$^{(a)}$	19,500$^{(a)}$	1.16	–	–
[3] oxidized	–	17,000$^{(a)}$	29,000$^{(a)}$	1.67	−1.28	108
[4]	AIBN	9700$^{(b)}$	16,000$^{(b)}$	1.65	–	–
[4] oxidized	–	13,200$^{(b)}$	26,100$^{(b)}$	1.98	−1.66	117
[5]	AIBN	8200$^{(b)}$	9300$^{(b)}$	1.05	–	–
[5] oxidized	–	6500$^{(b)}$	8100$^{(b)}$	1.24	−1.78; −1.45	130
[6]	Methyl-2-phenyloxirane, $TiCl_4$	11,400$^{(a)}$	14,600$^{(a)}$	1.28	−1.69	103
[7]	AIBN	20,000$^{(b)}$	22,400$^{(b)}$	1.12	–	–
[7] oxidized	–	20,900$^{(b)}$	29,900$^{(b)}$	1.43	−1.34	107

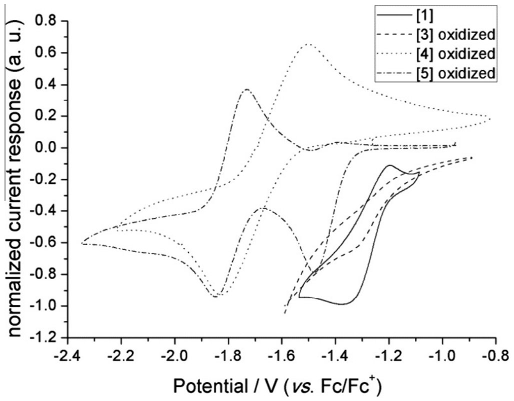


Fig. 1. Cyclic voltammogramms of polymer [1] and oxidized polymers [3,4,5] (0.1 V/s; 0.1 M Bu_4NPF_6 in DMF).

carefully ground in a mortar. *N*-Methyl-2-pyrrolidone was added to give a paste. This was kneaded further using a mortar. Subsequently, the paste was spread on a graphite sheet using a steel template (area: 1.5 cm^2). The fabricated electrode was dried under reduced pressure at 40 °C overnight and subsequently used to measure cyclic voltammetry. Oxidized polymer [7] possesses a similar structure to polymer [1] and displays its redox potential at −1.34 V (*vs.* Fc/Fc$^+$), with stable reduction and oxidation behavior over several cycles.

The reduction reaction of the oxidized polymer [3] could be observed at −1.28 V (*vs.* Fc/Fc$^+$), but unfortunately no re-oxidation was detected (Fig. 1). This may stem from the poly–vinyl backbone in *para*-position to the radical, which is unable to stabilize the reduced species [14]. In comparison to nitroxide-containing polymers in literature the described compounds exhibit a lower redox-potential. Most known nitroxides possess redox-potentials close to 0.3 V (*vs.* Fc/Fc$^+$) and only few, *e.g.*, aryl-nitroxides substituted with CF_3-groups show lower redox-potentials at around −1.1 V (*vs.* Fc/Fc$^+$). Like those the here described nitroxides are stable for several cycles at an even lower redox-potential [2,3]. In combination with a cathode this may allow for the fabrication of batteries with higher voltage than compared to the previously described nitroxides. The theoretical capacities of these polymers for a use in batteries are described in Table 1. The radical-concentrations of the polymers could be determined *via* the spin concentration obtained by ESR-experiments (70–85%).

4. Conclusion

Seven different polymers containing a redox-active n-type nitroxide have been synthesized and characterized. The synthetic strategy started from the respective amines, which were functionalized with methacrylic, *iso*-butylene or *tert*-butyl units. Methacrylamide- and styrene-containing monomers were polymerized *via* free-radical polymerization and oxidized to their nitroxide-form afterwards. *iso*-Butylene containing monomers, however, were oxidized to the stable nitroxides and polymerized as such *via* the cationic polymerization technique.

All polymers were investigated for their electrochemical activity and most polymers showed stable redox-behavior over several cycles at potentials of −1.3 V (*vs.* Fc/Fc$^+$) and lower.

These nitroxides, substituted with electron-withdrawing groups, possess redox-potentials lower than many of the commonly used nitroxide-radicals and represent interesting candidates for redox-active polymers (*e.g.*, for organic radical batteries). In the future we plan to test these polymers as electrodes in all-organic radical batteries.

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References

[1] Tebben L, Studer A. Angew Chem Int Ed 2011;50:5034–68.
[2] Janoschka T, Hager MD, Schubert US. Adv Mater 2012;24:6397–409.
[3] Oyaizu K, Nishide H. Adv Mater 2009;21:2339–44.
[4] Studer A, Schulte T. Chem Rec 2005;5:27–35.
[5] Wu Y, Bi L, Bi W, Li Z, Zhao M, Wang C, et al. Bioorg Med Chem 2006;14:5711–20.
[6] Nakahara K, Iwasa S, Satoh M, Morioka Y, Iriyama J, Suguro M, et al. Chem Phys Lett 2002:351–4.
[7] Piloty O, Schwerin BG. Ber Dtsch Chem Gesell 1901;34:1870–87.

[8] Koshika K, Chikushi N, Sano N, Oyaizu K, Nishide H. Green Chem 2010;12:1573–5.
[9] Koshika K, Sano N, Oyaizu K, Nishide H. Chem Commun 2009:836–8.
[10] Suguro M, Mori A, Iwasa S, Nakahara K, Nakano K. Macromol Chem Phys 2009;210:1402–7.
[11] Janoschka T, Teichler A, Häupler B, Jähnert T, Hager MD, Schubert US. Adv Energy Mater 2013;3:1025–8.
[12] Janoschka T, Teichler A, Krieg A, Hager MD, Schubert US. J Polym Sci Part A: Polym Chem 2012;50:1394–407.
[13] Grubbs RB. Polym Rev 2011;51:104–37.
[14] Hicks RG. Org Biomol Chem 2007;5:1321–38.
[15] Oyaizu K, Kawamoto T, Suga T, Nishide H. Macromolecules 2010;43:10382–9.
[16] Nishide H, Koshika K, Oyaizu K. Pure Appl Chem 2009;81:1961–70.
[17] Yonekuta Y, Susuki K, Oyaizu K, Honda K, Nishide H. J Am Chem Soc 2007;129:14128–9.
[18] Iwasa S, Suguro M, Natori N, Nakahara K, Iriyama J, Satoh M, et al. Electrochim Acta 2004;50:827–31.
[19] Marx L, Hemery P. Polymer 2009;50:2752–61.
[20] Flakus S, Mandel K, Bartsch M, Schmidt-Naake G. Macromol Rapid Commun 2005;26:1698–703.
[21] Jähnert T, Häupler B, Janoschka T, Hager MD, Schubert US. Macromol Chem Phys 2013;214:2616–23.
[22] Jähnert T, Häupler B, Janoschka T, Hager MD, Schubert US. Macromol Rapid Commun 2014;35:882–7.

Publication P4

P4) “Reactive inkjet printing of cathodes for organic radical batteries“

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Reactive Inkjet Printing of Cathodes for Organic Radical Batteries

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Mobile electrical appliances perpetually require improved batteries. For lightweight and flexible low-cost applications, batteries have to become thin, easy to produce, and also flexible. In this context, printing technology could pave the way for the cost-efficient manufacturing of flexible batteries – comparable to the production of organic solar cells.[1,2] While printed organic electronics, like organic photovoltaic-powered electrochromic displays[3] or LED lamps,[4] receive significant attention, these devices lack flexible organic energy storage and still employ traditional battery concepts.[5]

Most (printed) batteries rely on metal-based electrode materials, which often show unwanted environmental properties (e.g., release of toxic waste upon mining of metal ores, from landfill disposal sites, and municipal waste combustors); the rapidly evolving class of organic radical batteries (ORB) employs organic polymers as active electrode material.[6–8] A general problem of printed batteries is the cathode material. In primary cells, the use of manganese dioxide ($MnO_2|Zn$) is widespread, while secondary cells often employ lithium cobalt oxide ($LiCoO_2|Li$) or nickel oxyhydroxide (NiOOH|MH). Organic radical batteries, on the other hand, make use of a more environmentally favorable (polymeric) material that carries redoxactive stable radicals, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), **Scheme 1**. The increasing interest in this new class of fast charging, high rate/load capable batteries is reflected in numerous studies with their major focus ranging from polymer design (poly(methacrylate)s,[9,10] poly(norbornene)s[11] etc.) and electrolytes (organic carbonates,[9] water,[12] ionic liquid)[11] to the use of suitable conductive additives (vapor grown carbon fibers (VGCF),[13] graphite,[9] graphene).[14] On the other hand, up to now, only little attention was paid to the processing of these materials. Simple, solution-based wet processing techniques like spin-coating[15] and doctor blading[16] are generally employed for the fabrication of ORB electrodes. The disadvantages of such techniques – their tendency to waste much of the employed material and the inflexibility in shape and size of the electrode layout – encouraged us to look for an improved methodology. Advanced processing techniques such as inkjet printing, being contactless and highly flexible, can greatly improve the manufacturing of organic radical battery electrodes. Due to its additive nature, inkjet printing permits easy patterning and layered deposition of materials.

When taking the research from material design to device/electrode design, reconsideration of the polymer composition becomes necessary. On the one hand, the polymer needs to be highly soluble in solvents, which are suitable for the inkjet printing process. Typically, high boiling point solvents (>100 °C) such as chlorobenzene reveal a reliable droplet formation and good rheological properties of the ink.[17] On the other hand, the polymer has to be insoluble in the electrolyte solution (e.g., organic carbonates, acetonitrile) employed in the assembled device.

As shown earlier, electroactive radical polymers can be inkjet printed.[17] Nevertheless, the requirement in good solubility, i.e., low and controlled molar mass, renders the printed films useless, as the polymer films are readily soluble in the organic electrolyte solutions commonly used in ORBs. The charge storage capacity is completely lost after only two charging/discharging cycles.

In order to overcome this predicament, defined low molar mass polymers need to be prepared, printed, and subsequently crosslinked in order to provide sufficient stability of the electrode.

As commonly employed ORB polymers, such as the polyradical poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA), are poor electric conductors, the polymers need to be mixed with conductive additives such as graphite.[9] The inkjet printing and subsequent crosslinking of such composites is a highly demanding task. Numerous crosslinking techniques, which have been described before, are incompatible with the printing process. In situ crosslinking during the polymerization process, as described for the copolymerization with multifunctional co-monomers,[18,19] is not an option for inkjet printing due to the insolubility of these materials. In addition, approaches based on photocrosslinking, e.g., of TEMPO-substituted poly(norbornene)s, also work insufficiently with black colored, strongly light absorbing graphite/polymer composites.[19,20] One possible option to overcome this problem is to introduce a polymerizable co-monomer in the ORB polymer, printing this co-polymer and, subsequently, initiating the crosslinking process by an external stimulus (e.g., heat). The

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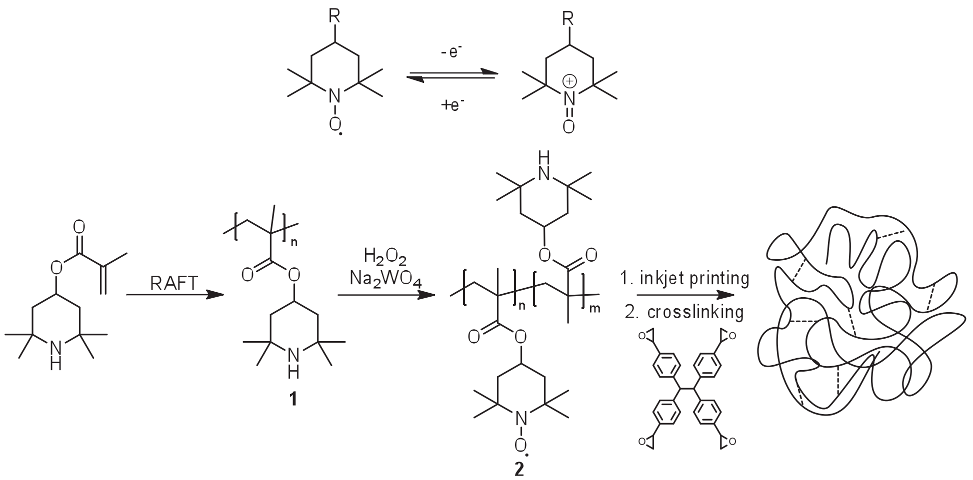

Scheme 1. Schematic representation of the reversible redox reaction of a TEMPO radical (top). Schematic representation of the synthesis of radical polymer poly(2,2,6,6-tetramethyl-piperidinyloxy-4-yl methacrylate) (PTMA) by RAFT polymerization, oxidation, and subsequent thermal crosslinking with a multifunctional epoxide (bottom).

disadvantages of this methodology are numerous: a) The co-monomer needs to have two orthogonal polymerizable groups; b) The preparation of co-polymers is more laborious than of simple homo-polymers; c) The initiator needed to start the crosslinking reaction contaminates the electrode composite and may have disadvantageous effects on its electro chemistry; d) Obviously, simple radical-induced methods are not suitable due to the presence of the free TEMPO radical.

For these reasons, we have developed a simple crosslinking approach that is compatible with inkjet printing and does neither require an additional initiator nor the preparation of a co-polymer. This reactive inkjet printing approach is based on the printing of a functional redoxactive polymer and the corresponding crosslinker. For a recent overview on reactive inkjet printing, see a feature article by Smith and Morrin.[21]

Crosslinking method: The TEMPO radical based polymer PTMA, the most promising of the studied radical polymers in terms of preparation and stability, is commonly prepared from the monomer 2,2,6,6-tetramethylpiperidin-4-yl methacrylate by free radical polymerization and subsequent oxidation of the amine bearing pre-polymer **1** in order to form the redoxactive TEMPO radical bearing polymer **2**.[9,10,14,22,23] If the oxidation step, affected by *m*-chloroperbenzoic acid[9] or hydrogen peroxide,[10] is incomplete a co-polymer is obtained (Scheme 1). The residual amino moieties, which are not oxidized to the nitroxide radicals, can therefore be used for further functionalization or crosslinking.

In order to avoid the use of additional initiators multifunctional epoxides (Scheme 1) were chosen as crosslinking agent. Epoxides readily react with amines and can therefore affect the crosslinking of the radical polymer. Since the polymer shows a good thermal stability (decomposition above 200 °C), the crosslinking could easily be initiated by thermal treatment of the printed patterns.

For inkjet printing the polymer needs to be readily soluble and the solutions require good rheological behavior (viscosity: 0.4 to 20 mPas). For this reason, reversible addition-fragmentation chain transfer (RAFT) polymerization was used as controlled radical polymerization technique to prepare the polymers.[17]

Ink formulation: An ink is commonly made of a solvent and the polymer that is to be printed. For ORB-electrodes the ink has to contain a conductive additive as well. Additives, such as VGCF[13] and graphite,[9] are commonly used in literature. For inkjet printing these materials proved to be unsuitable, as they cause clogging of the printing nozzle (inner diameter 70 µm). Carbon nanopowder, a material of much lower particle size (<50 nm), was found to be best suited. PTMA is well soluble in many solvents, including dichloromethane, acetonitrile, toluene, *N,N*-dimethylformamide (DMF), *o*-dichlorobenzene, and *N*-methyl-2-pyrrolidone (NMP). Several combinations of these solvents were tested. DMF was found to be most suitable, because it not only dissolves PTMA but also forms excellent dispersions of the carbon nanopowder. Since inkjet printing from a single solvent causes the preferential accumulation of the ink material at the rim of a dried film (coffee-ring-effect),[24] a co-solvent (NMP) in a content of 10 vol.% was added. As a result, the deposited material is homogeneously distributed all over the film. The dispersions made of other solvents were not sufficiently stable to permit inkjet printing.

Besides the active polymer and the conductive additive the crosslinking agent is the most important component of the ink. To ensure a high degree of crosslinking tetraphenylolethane glycidyl ether was chosen, as it can react with up to four amines. As materials inkjet printed from the described ink caused the formation of brittle films, which peel off in the electrolyte solution, a plasticizer (ethylene carbonate (EC)) was used. Upon addition of EC to the prescribed ink formulation in an amount of 5 vol.%, a homogeneous and stable film was formed. Ethylene carbonate, as many other organic carbonates used in battery applications, is electrochemically inert within a broad voltage window. It not only facilitates the formation of stable films but is also miscible with the electrolyte solution used in battery cycling experiments as well, thereby promoting the penetration of the polymer electrode film with the electrolyte.

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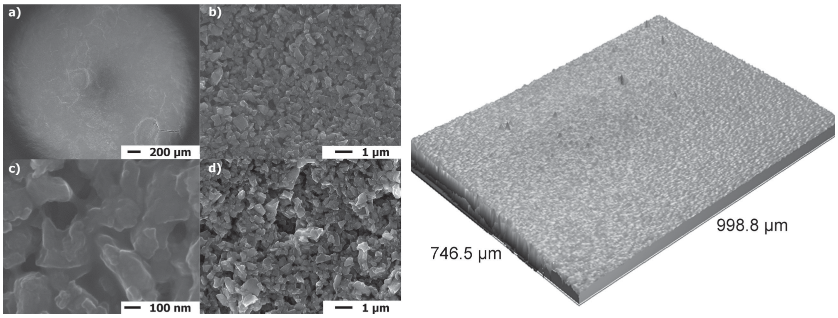

Figure 1. SEM micrographs of inkjet printed PTMA/carbon-nano-powder composite electrodes, (a-c) before charging/discharging, (d) after charging/discharging (left). Optical profiler image of a crosslinked inkjet printed film (right). Ink composition: active polymer PTMA (concentration: 5 mg/mL), crosslinking agent tetraphenylolethane glycidyl ether (concentration: 0.7 mg mL^{-1}), and solvent mixture DMF/NMP in a ratio of 9:1.

Electrochemical studies: In order to study the stability of the inkjet printed electrodes half-cells were built and charged/discharged repeatedly. The experiments were carried out in a temperature controlled cell at 30 °C employing a three electrode setup (Ag/AgCl reference electrode, platinum counter electrode, printed working electrode) and a 0.1 M solution of tetrabutylammonium hexafluorophosphate in propylene carbonate as electrolyte.

Inks that did not contain a crosslinking agent revealed a fast decrease in charge storage capacity. After only two cycles no active polymer was left. The stability of the electrode was enhanced by crosslinking the electrode using the optimized procedure described above. About 75% of the initial capacity was retained after 150 charging/discharging cycles. The decline can be attributed to a slow degradation of the electrode due to active polymer being washed out of the polymer composite. Scanning electron microscope (SEM) pictures of the cycled electrodes reveal minor changes in the electrode's surface morphology (**Figure 1**b/d). Because high molar mass/insoluble PTMA polymer can be considered electrochemically stable[6–8] and cyclic voltammetry (CV) experiments confirm that even an excess of the epoxy-crosslinker does not influence the redox chemistry of the polymer, the electrode's stability is most likely limited due to the necessity of crosslinking. Even an increase of the amount of the epoxide-crosslinker as well as using PTMA with up to 40% of free amine groups (60% oxidized to form TEMPO) did not result in a significantly improved stability. About carbon/epoxy resin composites it is known that the interfacial contact between the high surface area of carbon and the crosslinking agents strongly affect the kinetics and the final crosslinking state.[25–27] As the carbon nanopowder appears to be affecting the crosslinking process, epoxidized carbon nanopowder was prepared by reacting the virgin powder with *m*-chloroperoxybenzoic acid.[28] The epoxidized carbon can react with the free amine groups of the PTMA polymer and act as crosslinking agent itself, covalently linking the active polymer to the insoluble conductive additive. Thereby an increased cycling stability was achieved (**Figure 2**). After a slight increase of the charge storage capacity within the first cycles due to wetting/activation of the electrode the initial capacity was retained even after 150 cycles.

Subsequently, a beaker type battery consisting of a printed polymer composite cathode, a zinc-anode, and a $ZnBF_4$-electrolyte in propylene carbonate was assembled. The cell exhibits an average discharge voltage of 1.25 V and a capacity of 20.5 µAh (ca. 50 mAh g^{-1}, theor. capacity of the polymer is 66 mAh g^{-1}).

In summary, a reactive inkjet printing strategy for the manufacturing of printed electrodes used in organic radical batteries was developed. Being contactless and highly flexible inkjet printing is superior to conventional solution-based wet processing techniques. The low molar mass, electroactive polyradical poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA), that was used for inkjet printing, was prepared by RAFT-polymerization and a subsequent partial oxidation. The incomplete oxidation is an easy way of obtaining a reactive copolymer, which not only bears electroactive sites but also chemically reactive amine groups; advanced co-polymerization strategies are not necessary. An optimized ink containing the electro active polymer, an epoxy-based crosslinker, carbon nanopowder, and additives/solvents was developed and inkjet printed. Electrodes of good stability, as proven by repeated charging/discharging experiments, were prepared by initiator-free, thermal

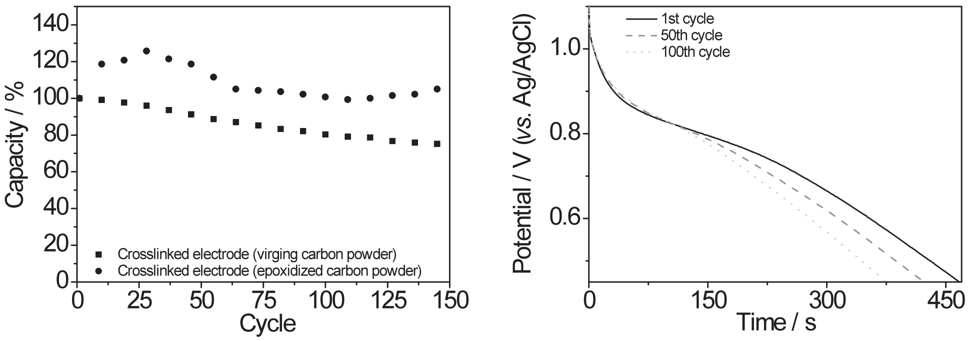

Figure 2. Cycling stability of inkjet printed electrodes at 1.5 A m^{-2} over 150 cycles (left). Discharging curves of inkjet printed electrodes at 1.5 A m^{-2} using a solution of tetrabutylammonium hexafluorophosphate in propylene carbonate as electrolyte (right).

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crosslinking of the free amine-bearing PTMA and the epoxy-based crosslinker. By employing epoxidized carbon nanopowder as chemically reactive conductive additive a further improvement could be observed. The printed electrodes are stable for over one hundred cycles. This technique might be of interest for the manufacturing of patterned, flexible organic radical batteries used in sensor devices, smart packaging, DNA chips, or battery-powered smart cards.

Experimental Section

Synthesis: PTMA was prepared according to literature by means of RAFT polymerization and subsequent oxidation with hydrogen peroxide and a sodium tungstate catalyst.[17]

Polymer 1: $M_n = 35{,}600$ g mol^{-1}, $M_w = 39{,}800$ g mol^{-1}, $M_w/M_n = 1.12$, amine/nitroxide radical ratio = 2/8.

Polymer 2: $M_n = 51{,}000$ g mol^{-1}, $M_w = 58{,}200$ g mol^{-1}, $M_w/M_n = 1.14$, amine/nitroxide radical ratio = 4/6.

The polymer's degree of nitroxide radical functionalization was determined using UV-vis spectroscopy[19] (280 nm) on a Perkin-Elmer Lamda-45 UV-vis spectro-photometer at room temperature in tetrahydrofurane (1 cm cuvettes). A fully functionalized PTMA prepared by group transfer polymerization was used as reference standard.

Molar masses were determined by size exclusion chromatography (SEC): Agilent 1200 series system (degasser: Polymer Standard Service Mainz, pump: G1310A, auto sampler: G1329A, oven: Techlab, diode array detector: G1315D, RI detector: G1362A) using a pC/PSS GRAM 1000/30 Å column and dimethylacetamide (+0.21% lithium chloride) as eluent at a flow rate of 1 mL/min (40 °C).

Carbon nanopowder (Aldrich) was epoxidized by refluxing with *m*-chloroperoxybenzoic acid in dichloromethane.[28]

Electrochemical characterization: A Princeton Applied Research VersaSTAT potentiostat/galvanostat was used for all charging/discharging experiments. The experiments were carried out in a temperature controlled cell (30 °C) using an Ag/AgCl reference electrode and a platinum counter electrode. A 0.1 M solution of tetrabutylammonium hexafluorophosphate in propylene carbonate was used as electrolyte. Before the first charging the printed electrodes were immersed in the electrolyte until a constant open current potential was observed.

Inkjet printing: Inkjet printing was performed using an Autodrop professional system from microdrop technologies (Norderstedt, Germany). The printer was equipped with a micropipette with an inner diameter of 70 µm. The carbon nanopowder (particle size < 50 nm, Aldrich) dispersion was prepared by ultrasonication for 5 h in the solvent system *N,N*-dimethylformamide/*N*-methyl-2-pyrrolidone 90/10. Afterwards the dispersion was filtered by a syringe filter (pore size: 5 µm) to prevent nozzle clogging. The ink was prepared by addition of the dissolved polymer (concentration: 5 mg/mL), the crosslinking agent tetraphenylolethane glycidyl ether and the plasticizer ethylenecarbonate (5 vol.%). The ink contained the polymer and the carbon nanopowder in a ratio of 1/1 by weight. The content of crosslinker was varied according to the content of free amine groups of PTMA. Printing was performed by using a drop count of 100 drops, a dot spacing of 100 µm, a printing speed of 20 mm/s and a substrate temperature of 50 °C. As substrate a graphite foil was used. After drying of the film at 50 °C, crosslinking was carried out for 12 h at 130 °C in an oven.

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[1] F. C. Krebs, *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 394–412.
[2] D. Angmo, T. T. Larsen-Olsen, M. Jorgensen, R. R. Sondergaard, F. C. Krebs, *Adv. Energ. Mat.* **2013**, *3*, 172–175.
[3] J. Jensen, H. F. Dam, J. R. Reynolds, A. L. Dyer, F. C. Krebs, *J. Polym. Sci., Part B: Polym. Phys.* **2012**, *50*, 536–545.
[4] F. C. Krebs, T. D. Nielsen, J. Fyenbo, M. Wadstrom, M. S. Pedersen, *Energy Environ. Sci.* **2010**, *3*, 512–525.
[5] F. C. Krebs, J. Fyenbo, D. M. Tanenbaum, S. A. Gevorgyan, R. Andriessen, B. van Remoortere, Y. Galagan, M. Jorgensen, *Energy Environ. Sci.* **2011**, *4*, 4116–4123.
[6] K. Oyaizu, H. Nishide, *Adv. Mater.* **2009**, *21*, 2339–2344.
[7] K. Nakahara, K. Oyaizu, H. Nishide, *Chem. Lett.* **2011**, *40*, 222–227.
[8] T. Janoschka, M. D. Hager, U. S. Schubert, *Adv. Mater.* **2012**, *24*, 6397–6409.
[9] K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, J. Iriyama, M. Suguro, E. Hasegawa, *Chem. Phys. Lett.* **2002**, *359*, 351–354.
[10] Y. Kim, C. Jo, J. Lee, C. W. Lee, S. Yoon, *J. Mater. Chem.* **2012**, *22*, 1453–1458.
[11] D. Yang, Z. Yixiao, G. Lei, X. Guofeng, X. Jingying, *J. Electrochem. Soc.* **2011**, *158*, A291–A295.
[12] K. Koshika, N. Sano, K. Oyaizu, H. Nishide, *Chem. Commun.* **2009**, *45*, 836–838.
[13] K. Nakahara, J. Iriyama, S. Iwasa, M. Suguro, M. Satoh, E. J. Cairns, *J. Power Sources* **2007**, *163*, 1110–1113.
[14] W. Guo, Y.-X. Yin, S. Xin, Y.-G. Guo, L.-J. Wan, *Energy Environ. Sci.* **2012**, *5*, 5221–5225.
[15] K. Koshika, N. Sano, K. Oyaizu, H. Nishide, *Macromol. Chem. Phys.* **2009**, *210*, 1989–1995.
[16] Y.-Y. Cheng, C.-C. Li, J.-T. Lee, *Electrochim. Acta* **2012**, *66*, 332–339.
[17] T. Janoschka, A. Teichler, A. Krieg, M. D. Hager, U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 1394–1407.
[18] T. Ibe, R. B. Frings, A. Lachowicz, S. Kyo, H. Nishide, *Chem. Commun.* **2010**, *46*, 3475–3477.
[19] L. Bugnon, C. J. H. Morton, P. Novak, J. Vetter, P. Nesvadba, *Chem. Mater.* **2007**, *19*, 2910–2914.
[20] T. Suga, H. Konishi, H. Nishide, *Chem. Commun.* **2007**, *43*, 1730–1732.
[21] P. J. Smith, A. Morrin, *J. Mater. Chem.* **2012**, *22*, 10965–10970.
[22] H. Nishide, S. Iwasa, Y. J. Pu, T. Suga, K. Nakahara, M. Satoh, *Electrochim. Acta* **2004**, *50*, 827–831.
[23] K. Nakahara, J. Iriyama, S. Iwasa, M. Suguro, M. Satoh, E. J. Cairns, *J. Power Sources* **2007**, *165*, 398–402.
[24] E. Tekin, B. J. de Gans, U. S. Schubert, *J. Mater. Chem.* **2004**, *14*, 2627–2632.
[25] A. Garton, W. T. K. Stevenson, S. P. Wang, *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 1377–1391.
[26] M. A. Andres, R. Miguez, M. A. Corcuera, I. Mondragon, *Polym. Int.* **1994**, *35*, 345–353.
[27] D. Puglia, L. Valentini, J. M. Kenny, *J. Appl. Polym. Sci.* **2003**, *88*, 452–458.
[28] W. Yuan, M. B. Chan-Park, *ACS Appl. Mater. Interfaces* **2012**, *4*, 2065–2073.

Publication P5

P5) “Poly(methacrylates) with pendant benzoquinone units – monomer synthesis, polymerization, and electrochemical behavior: Potential new polymer systems for organic batteries“

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Poly(methacrylates) with Pendant Benzoquinone Units – Monomer Synthesis, Polymerization, and Electrochemical Behavior: Potential New Polymer Systems for Organic Batteries

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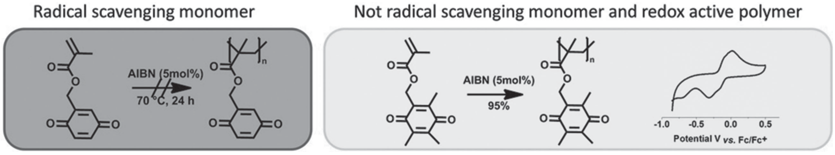
Redox-active polymers became the focus of attention in the field of organic electronics during the last decade. Quinoide systems are intensively studied in this field. Although benzoquinones are generally known as radical scavengers, certain monomers can be polymerized by radical polymerization techniques. For this purpose, methacrylate functionalities are attached to the redox-active quinone moiety. A free-radical polymerization technique is applied utilizing AIBN as initiator. The molar mass can be adjusted by the choice of an appropriate solvent system. Electrochemical investigations of these new monomers and polymers, in particular cyclic voltammetry, are performed in aqueous and non-aqueous electrolytes in the dissolved and solid states, showing the potential usefulness of the system for applications in organic radical batteries.



1. Introduction

Quinone-containing polymers have been investigated in different fields of chemistry and material science in the last decades due to their interesting electrochemical properties.[1] A reversible two-electron redox behavior can be observed, whereas the redox potential can be altered by the introduction of different substituents.[2] Additionally, the electrochemical behavior of quinone moieties strongly depends on the chemical environment (e.g., the electrolyte, the conducting salts, etc.). In organic solutions, the reduction proceeds in two separate one-electron reactions over the semiquinone intermediate to the hydroquinone. In contrast, the reduction in aqueous solution is dependent on the pH value; in acidic solutions, it follows the one electron reduction – hydrogen transfer (EHEH) mechanism (i.e., protonation after one-electron reduction). Under basic conditions, only one two-electron reaction is observed (i.e., simultaneous reduction of both carbonyl groups).[3] Noteworthy, quinones feature a high chemical robustness in combination with a low molar masses (ca. 120 g mol^{-1} dependent on the substitution pattern). As a consequence, they have been applied for analytical systems,[4] as capacitor material,[5] redox resin,[6] as well as active anode

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material for organic batteries[7] and photorechargeable batteries.[8] For the majority of these applications, insolubility of the corresponding material is required. Thus, controlled and/or living polymerization procedures are disregarded. Polymers containing in chain quinone moieties are widely known.[1,9,10] In contrast, polymers with pendant quinone units are less investigated. Typical living polymerization techniques (e.g., living anionic or cationic polymerization) are not suitable for the synthesis of high molar mass polymers due to incompatibility of the quinone carbonyl moiety to the initiating and/or propagating species in the reaction mechanism. In addition, quinones commonly act as radical scavengers; hence, a radical polymerization of unprotected benzoquinone-containing monomers has not been accomplished so far. The two main strategies to overcome this drawback have either been the usage of protection groups,[11,12] or the introduction of the quinone unit via a polymer analogous reaction.[13,14] Both synthetic strategies do not ensure a complete functionalization of the polymer.

In this contribution, the design of a fully methyl-substituted benzoquinone methacrylate monomer is displayed. By the introduction of methyl groups to the benzoquinone core in the 2-, 3-, or 5-position, a potential radical formation is suppressed. The application of a free-radical polymerization technique yields quinone pendant polymers with high molar masses. Furthermore, the influence of different solvents on the polymerization behavior as well as the electrochemical characterization of the resulting polymers in various electrolytes is investigated.

2. Experimental Section

2.1. Materials

All reagents were obtained from commercial sources and used as received unless otherwise noted. Solvents were dried according to standard procedures. Dry THF and dichloromethane were obtained from a Pure Solv MD-4-EN solvent purification system. 2,5-Dimethoxybenzalcohol[15] and 1,4-dimethoxy-2,3,5-trimethylbenzene[16] were synthesized according to the literature.

Reactions were monitored by TLC (aluminum sheets coated with silica gel 60 F254 by Merck) and SECs for the polymers were measured with a Shimadzu SCL-10A VP controller, a LC-10AD pump, a RID-10A refractive index detector, a SPD-10AD VP UV-detector, and a PSS SDV prelin M (THF-N) column; temperature: 40 °C, eluent: THF; flow rate: 1 mL min^{-1}, calibration: polystyrene.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 300 (300 MHz) spectrometer at 298 K. Chemical shifts are reported in parts per million (ppm, δ scale) relative to the residual signal of the deuterated solvent.

Column chromatography was performed on silicagel 60 (Merck). Elemental analyses were carried out using a Vario ELIII – Elementar Euro and an EA – HekaTech.

Electrochemical measurements were performed on a Princeton Applied Research Versastat potentiostat with a standard three-electrode configuration using a glassy carbon-disk working electrode, a platinum-rod auxiliary electrode, and an Ag/AgCl reference electrode. The experiments were carried out in degassed solvents applying ferrocene as an internal standard.

2.2. Synthesis

2.2.1. Synthesis of 2,5-dimethoxybenzyl methacrylate (**1**)

2,5-Dimethoxybenzylalcohol 4.17 g (24.8 mmol) and 0.03 g (0.248 mmol) *N′*,*N′*-dimethylaminopyridine (DMAP) were dissolved in 250 mL of dichloromethane and 5.16 mL of triethylamine (37.2 mmol) was added. After cooling the reaction mixture to 0 °C, 3.45 mL of methacryloyl chloride (29.8 mmol) was added dropwise over a period of 20 min. The reaction mixture was stirred 1 h at 0 °C and 2 h at room temperature. 50 mL of saturated aqueous $NaHCO_3$ solution was added and the organic phase was separated, washed twice with water, once with brine, dried over sodium sulfated, and filtered. After evaporation of the solvent, 5.34 g (91%) of yellow oil was obtained.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.10; H, 6.91. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.55 (s, 3H); 6.15 (m, 1H); 5.55 (m, 1H); 5.4 (s, 2H); 3.70 (s, 6H); 1.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 167.2; 153.1; 149.0; 137.8; 128.2; 123.7; 114.3; 114.2; 112.3; 63.0; 56.1; 55.8; 17.9.

2.2.2. Synthesis of (3,6-dioxocyclohexa-1,4-dienyl)methyl methacrylate (**2**)

2,5-Dimethoxybenzyl methacrylate (0.94 g, 4.00 mmol) was dissolved in 20 mL of acetonitrile and a solution of 5.48 g of ceric(IV) ammonium nitrate (CAN) (10 mmol) was added. The reaction mixture was stirred for 1.5 h. Subsequently, 50 mL of water were added and the mixture was extracted three times with 20 mL of dichloromethane. The combined organic phases were dried over sodium sulfate, filtered and the solvent was evaporated under reduced pressure. The crude product was further purified using flash chromatography (hexane:ethyl acetate 4:1) to obtain 0.6 g (73%) of the methacrylate **2** as an orange solid.

Anal. Calcd. for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 64.10; H, 4.82. ^{1}H NMR ($CDCl_3$, 300 MHz): 6.79 (s, 1H); 6.76 (d, 1H) 6.69 (d, 1H), 6.22 (s, 1H) 5.68 (s, 1H), 1.99 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ = 187.2; 183.0; 169.3; 167.2; 137.8; 136.8; 134.4; 123.7; 61.9; 17.9.

2.2.3. Synthesis of 2,5-dimethoxy-3,4,6-trimethylbenzaldehyde (**3**)

2,5-Dimethoxy-3,4,6-trimethylbenzaldehyde was synthesized according to a modified procedure described in the literature.[11] Trifluoroacetic acid (271 mL) was added to a mixture of 1,4-dimethyl-2,3,5-trimethylbenzene (24.4 g, 135 mmol) and hexamethylenetetramine (19.0 g, 135 mmol). The mixture was stirred at reflux for 16 h and most of the solvent subsequently removed in vacuo. The oily residue was dissolved in 300 mL of dichloromethane and the resulting solution was washed three times with 300 mL water, once with saturated $NaHCO_3$ aqueous solution and once with brine. The organic phase was dried over sodium sulfate and filtered before solvent evaporation. The crude product was recrystallized from an ethanol/water mixture to obtain 22.4 g (79%) white needles.

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 65.10; H, 6.11. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 10.41$ (s, 1H); 3.70 (s, 3H); 3.58 (s, 3H); 2.42 (s, 3H); 2.19 (s, 3H); 2.13 (s, 3H). ^{13}C NMR ($CDCl_3$, 50.3 MHz): $\delta = 192.8$; 159.1; 153.6; 138.4; 131.9; 129.1; 126.3; 63.3; 60.3; 13.7; 12.8; 12.1.

2.2.4. Synthesis of 2,5-dimethoxy-3,4,6-trimethylbenzylalcohol (**4**)

3 (21.6 g, 104 mmol) was dissolved in 200 mL of methanol. The reaction mixture was cooled to 0 °C and sodium borohydride (4.32 g, 114 mmol) was added in portions. After stirring 4 h at room temperature, the solvent was evaporated and the residue was dissolved in 400 mL of dichloromethane and 200 mL of 2 M hydrochloric acid. The phases were separated and the organic phase was extracted twice with water (200 mL) and once with brine, dried over sodium sulfate, and the solvent was evaporated under reduced pressure. The crude product was purified by recrystallization from hexane to obtain 19.5 g (90%) of white powder.

Anal. Calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.21; H, 7.15. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 4.70$ (s, 2H); 3.72 (s, 3H); 3.64 (s, 3H); 2.31 (s, 3H); 2.25 (s, 1H); 2.19 (s, 3H); 2.17 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 153.3$; 153.2; 130.8; 130.0; 128.1; 61.5; 60.0; 57.7; 12.7; 12.5; 11.7.

2.2.5. Synthesis of 2,5-dimethoxy-3,4,6-trimethylbenzyl methacrylate (**5**)

2,5-Dimethoxy-3,4,6-trimethylbenzylalcohol (20 g, 95 mmol) and *N′N′*-dimethylaminopyridine (0.58 g, 4.76 mmol) were dissolved in 380 mL of dichloromethane and triethylamine (15.9 mL, 114 mmol, 1.2 equiv.) was added. The solution was cooled to 0 °C and methacryloyl chloride (11.93 g, 114 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was stirred 1 h at 0 °C and 2 h at room temperature. 50 mL of saturated aqueous $NaHCO_3$ solution was added and the organic phase was separated, washed twice with water, once with brine, dried over sodium sulfate, and filtered. After evaporation of the solvent and recrystallization from methanol, 25.2 g (91%) of a pale yellow powder was obtained.

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.09; H, 7.91. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 6.07$ (s, 1H); 5.53 (s, 1H); 5.27 (s, 2H); 3.68 (s, 3H); 3.66 (s, 1H); 2.25 (s, 3H); 2.22 (s, 3H); 2.19 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 167.2$; 150.1; 147.9; 137.8; 129.8; 128.2; 128.0; 123.7; 118.9; 60.8; 17.9; 15.6; 11.9.

2.2.6. Synthesis of (2,4,5-trimethyl-3,6-dioxocyclohexa-1,4-dien-1-yl)methyl methacrylate (**6**)

5 (2 g, 7.19 mmol) was dissolved in 24 mL of acetonitrile and an aqueous solution of ceric(IV) ammonium nitrate (8.67 g, 15.81 mmol) was added. The reaction mixture was stirred for 1.5 h. Then, 50 mL of water were added and it was extracted three times with 20 mL of diethylether. The combined organic phases were dried over sodium sulfate, filtered, and the solvent was evaporated. Subsequently, the crude product was purified using flash chromatography with dichloromethane as eluent to obtain 1.7 g (95%) of the methacrylate as a bright yellow solid.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.70; H, 6.48. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 6.05$ (s, 1H); 5.54 (s, 1H); 5.08 (s, 2H); 2.11 (s, 3H); 2.02 (s, 6H); 1.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 187.2$; 185.3; 167.2; 161.9; 143.6; 140.7; 137.8; 123.7; 55.7; 17.9.

2.2.7. General Procedure for Free-Radical Polymerization

The monomer **6** (100 mg, 0.403 mmol) and 3.3 mg AIBN (5 mol%) were dissolved in 0.2 mL solvent. The reaction solution was degassed by three freeze–pump–thaw cycles and then heated to 70 °C for 24 h. The conversion was examined with gas chromatography and anisole as internal standard. The reaction mixture was cooled to room temperature and the polymer **7** was obtained by precipitation from cold hexane.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.65; H, 6.42. NMR: ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 4.82$ (br, 2H); 2.10 (br, 9H); 1.71–0.82 (br, 3H).

2.2.8. General Procedure for Free-Radical Polymerization of Crosslinked Polymers **8**

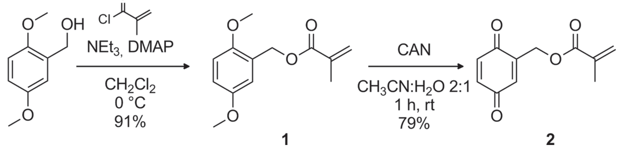
Monomer **6** (641 mg, 2.58 mmol), 37 mg ethylene(bisoxyethylene) methacrylate (0.129 mmol), and 21.2 mg AIBN (5 mol%) were dissolved in 1.3 mL solvent. The reaction solution was degassed by three freeze–pump–thaw cycles and then heated to 70 °C for 24 h. The reaction mixture was cooled to room temperature and the polymer **8** was obtained by precipitation from cold hexane.

^1H NMR ($CDCl_3$, 300 MHz): $\delta = 4.82$ (br); 4.31–4.25 (br); 3.71–3.38 (br); 2.10 (br); 1.71–0.82 (br).

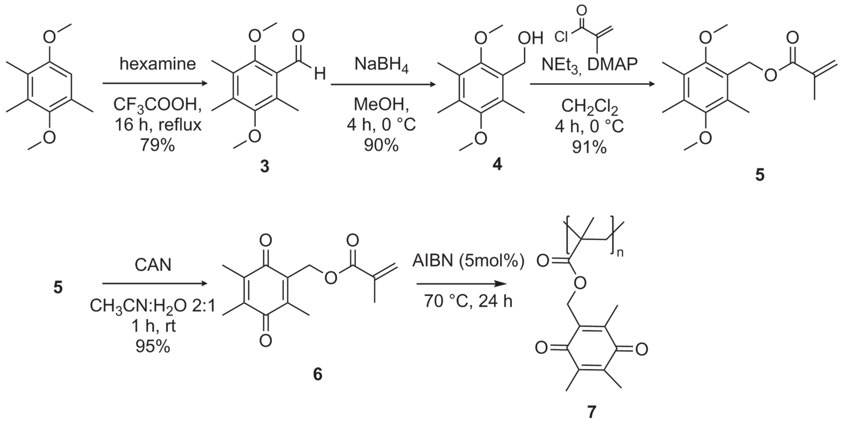
3. Results and Discussion

3.1. Synthesis

The unsubstituted benzoquinone methacrylate monomer (Scheme 1) was synthesized utilizing 2,5-dimethoxybenzylalcohol as starting material. Commercially available 2,5-dimethoxybenzylalcohol was treated with methacryloyl chloride to obtain the ester **1**. The methoxy-protecting groups were oxidatively cleaved by a slight



Scheme 1. Schematic representation of the synthesis of the unsubstituted monomer **2**.



Scheme 2. Schematic representation of the synthesis of monomer **6**.

excess of ceric(IV) ammonium nitrate (CAN) to obtain **2**. This synthesis was performed within two steps in excellent yields; however, the free-radical polymerization did not yield any polymer, even with 50 mol% AIBN as radical initiator in various solvents due to the radical scavenger properties of the benzoquinone structure.

In order to suppress this radical scavenging behavior, a fully methyl-substituted monomer was synthesized (Scheme 2). 2,3,5-Trimethylhydroquinone was chosen as starting material. The phenolic groups of the hydroquinone were in the first step protected as methoxy groups using dimethylsulfate, followed by the introduction of the formyl group applying a Duff reaction. The aldehyde **3** was reduced in the next step to the corresponding alcohol **4** using sodium borohydride as reducing agent, followed by *N*′,*N*′-dimethylaminopyridine-catalyzed esterification of the alcohol **4** with methylacryloyl chloride and the oxidative cleavage of the methoxy groups applying ceric(IV) ammonium nitrate as oxidant. The 2,3,5-methyl-substituted monomer **6** could be synthesized within five steps in high yield. The free-radical polymerization was carried out utilizing AIBN as initiator. First, the influence of the solvent on the degree of polymerization was investigated (Table 1). Therefore, the polymerization was carried out in solvents with different polarity utilizing 5 mol% of initiator to ensure that the amount of radicals is not the limiting factor (Scheme 3). In general, polymers with high molar mass and high monomer conversion were obtained in polar aprotic solvents such as *N,N*′-dimethylformamide or *N,N*′-dimethylacetamide. Polar protic, unpolar, and chlorinated solvents lead to lower conversion and lower molar mass (Table 1). 1,4-Dioxane gave the best results with regard to molar mass and monomer conversion.

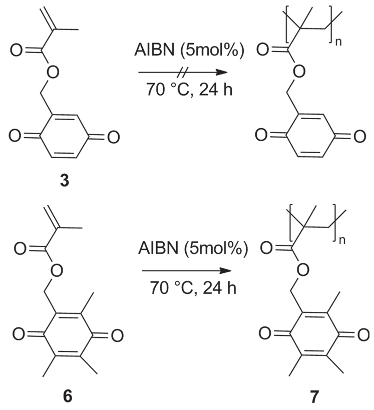
Secondly, the necessary amount of initiator was determined. Therefore, 1,4-dioxane was used as solvent and the molar percentage of initiator diversified between 1 and 10 mol% (Table 2). For high and full conversion, respectively, at least 5% of initiator was necessary. With less initiator, however, polymer can be obtained in moderate yields with low degree of polymerization. This reveals that the quinone unit still has limited radical-quenching abilities. Controlled radical polymerization techniques, like reversible addition–fragmentation chain transfer polymerization (RAFT), with a very low radical content could not be performed successfully.

Crosslinked polymers can be easily synthesized by statistical copolymerization of a bifunctional monomer with two polymerizable groups. As mentioned before, many applications rely on insoluble but swellable and therefore redox-active polymers.

A crosslinked polymer using a low ratio of a dimethylacrylate with a triglyme spacer was synthesized in excellent yield and conversion.

Table 1. Influence of the solvent on the polymerization.

Solvent	M_n [g mol^{-1}]	M_w [g mol^{-1}]	PDI	Conv. [%]
THF	6190	11 500	1.86	95
n-BuOH	2080	4410	2.18	62
DMAc	5200	9540	2.84	93
DMF	19 100	28 900	2.51	82
1,4-Dioxane	17 400	40 100	3.30	97
Toluene	11 800	22 200	2.04	81
1,2-Dichloroethane	4280	8990	2.10	84



Scheme 3. Schematic representation of polymerization of monomers **3** and **6**.

Table 2. Influence of the amount of initiator on the polymerization.

AIBN [mol%]	M_n [g mol^{-1}]	M_w [g mol^{-1}]	PDI	Conv. [%]
10	17 800	40 500	3.31	95
5	17 400	40 100	3.30	95
2	7 420	14 500	1.95	62
1	6 510	11 500	1.77	23

3.2. Electrochemistry

The electrochemical behavior of quinone systems has been investigated in detail. In organic solvents, they undergo in general two separate one-electron reactions: first, a one-electron-redox-reaction to the semiquinone, which is further reduced in a slow one-electron-redox-reaction to the corresponding dianion. Semiquinones are reported to be quite instable and readily undergo disproportion. Two semiquinones form irreversibly the chinhydrone, a charge transfer complex. In aqueous media, the redox behavior of quinone systems is strongly dependent on the pH value. In acidic and neutral media, the reduction works in general according the EHEH mechanism. Two rounds of electron transfers are coupled with two proton acceptances. The reduced form consists of the protonated hydroquinone. Under alkaline conditions, the reduction reveals a two-electron reduction in one wave resulting the corresponding dianion.[3]

The electrochemical behavior of the polymers was investigated utilizing cyclic voltammetry to examine the redox properties in different organic and aqueous solvents, with various conducting salts. Therefore, a solution of the polymer in DMF (1 mg mL^{-1}) was dropcasted onto a glassy carbon electrode and the solvent was evaporated at 80 °C.

The electrochemical behavior of the film (thickness: 50–250 nm) of polymer **7** in propylene carbonate exhibits two reduction waves at –0.34 and –1.21 V vs Fc/Fc$^+$ with

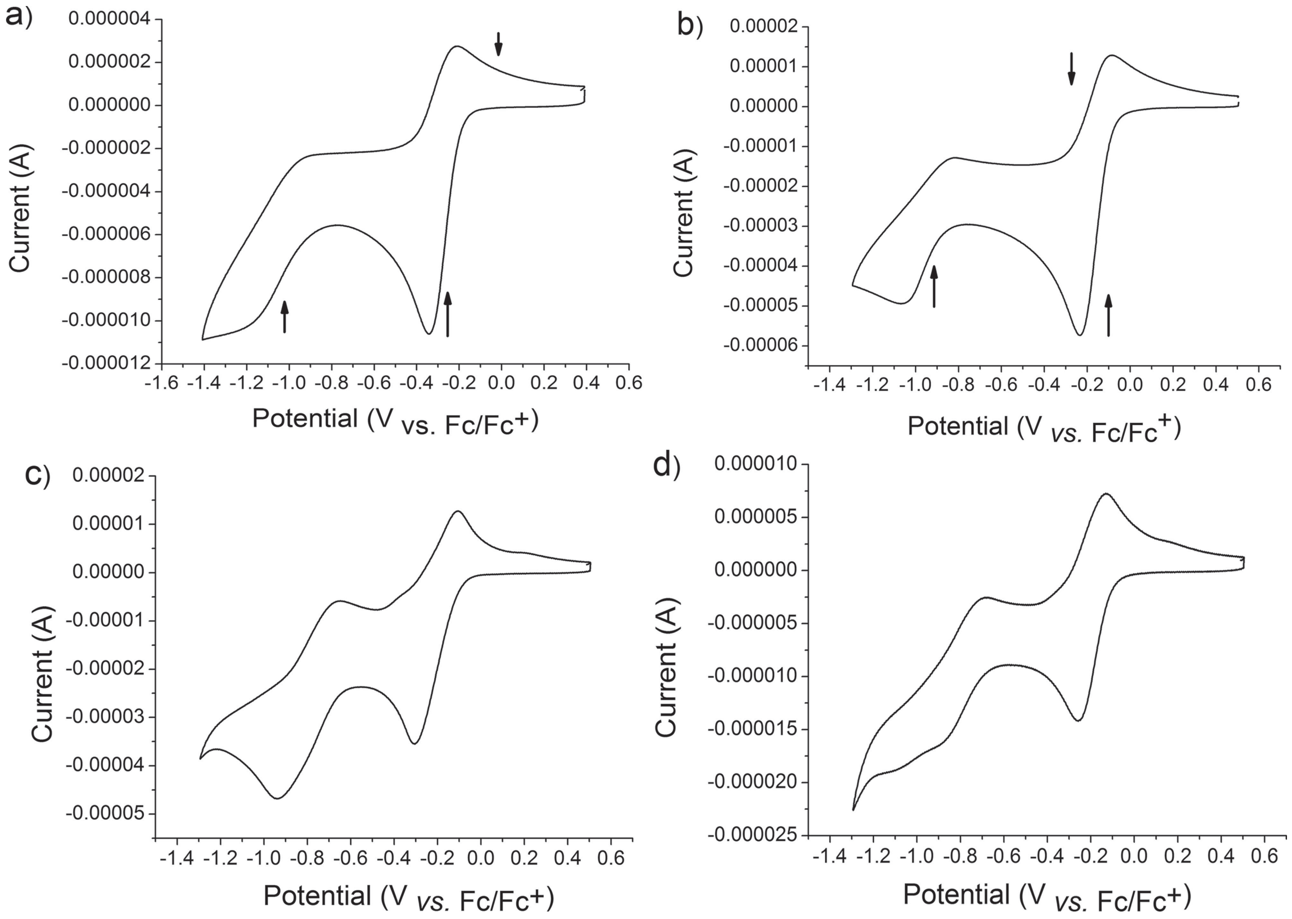


Figure 1. Cyclic voltammograms of monomer **6** and polymer **7** at rt; a) 20 × 10^{-3} M solution of **6** in acetonitrile, 0.1 M TBAClO$_4$, scan rate 0.1 V s^{-1}; b) 20 × 10^{-3} M solution of **6** in propylene carbonate, 0.1 M TBAClO$_4$, scan rate 0.1 V s^{-1}; c) 20 × 10^{-3} M solution of **6** in dichloromethane, 0.1 M TBAClO$_4$, scan rate 0.1 V s^{-1}; d) 20 × 10^{-3} M solution of **7** in dichloromethane, 0.1 M TBAClO$_4$, 0.1 V s^{-1}.

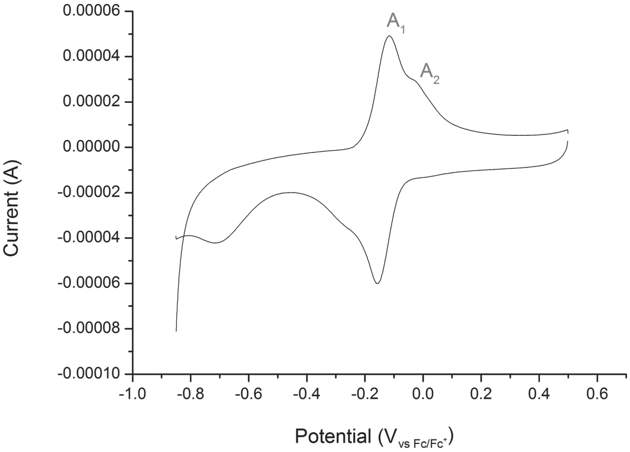


Figure 2. Cyclic voltammogram of polymer **7**, 0.1 M $HClO_4$, scan rate 0.01 V s^{-1}.

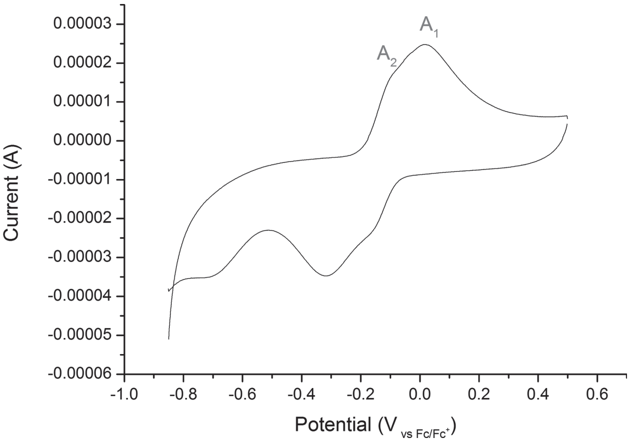


Figure 4. Cyclic voltammogram of polymer **6**, 0.1 M $HClO_4$, 0.01 V s^{-1}, rt.

steadily decreasing intensity over cycling, possibly because of the nucleophilic attack of the anion at the carbonyl carbon of propylene carbonate. The first reduction shows a limited reoxidation, the second reduction wave reveals irreversible reduction (Figure 1a). To investigate this further, an electrolyte was utilized that is inert toward a nucleophilic attack.

In acetonitrile, two irreversible redox reactions at –0.23 and –1.05 V vs Fc/Fc^+ with strongly decreasing intensity could be observed. A reoxidation with lower intensity is only observed for the first reduction wave (Figure 1b). Therefore, it can be assumed that the formed anion attacks the pendant ester functionality. The addition of Li salts like $LiClO_4$ to the electrolyte that should inhibit the nucleophilic attack leads to a non-reversible redox behavior of the quinone unit, which cannot be explained further. Both monomer **6** and polymer **7** reveal a similar electrochemical behavior in dichloromethane solution. Monomer **6** exhibits two redox reactions occurring at –0.20 and –0.80 V vs Fc/Fc^+ (Figure 1c) and polymer **7** reveals two redox reactions at –0.20 and –0.79 V vs Fc/Fc^+ (Figure 1d). In both cases, the first redox reaction reveals a quasi-reversible redox reaction. The second reduction is irreversible.

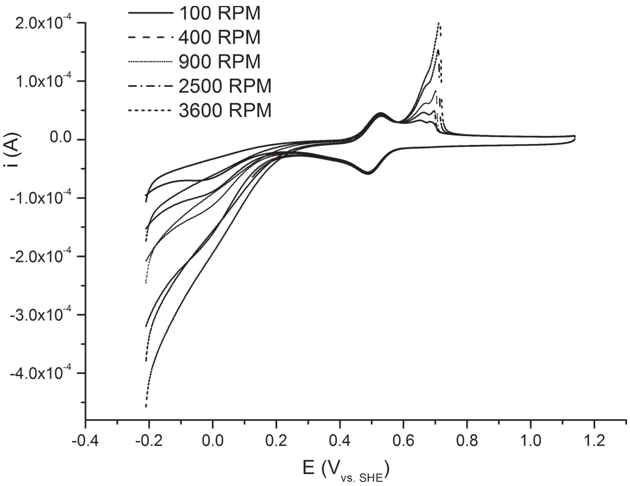


Figure 3. Cyclic voltammogram of polymer **7** in 0.1 M $HClO_4$, scan rate 10 mV s^{-1} rotation speed: 100 to 3600 RPM.

Polymer **7** was stable under acidic conditions and we were able to measure dropcasted films in 0.1 M aqueous $HClO_4$ as electrolyte. Surprisingly, the polymer exhibits one two-electron wave occurring at around 0.15 V vs SHE, which could be separated at lower scan rates (Figure 2). The intensity of the signals is stable over more than 100 cycles. Therefore, it can be assumed that the nucleophilic attack of the phenolate is inhibited by protonation.

Further investigations applying rotating disk electrode technique revealed that the first reduction wave at 0.51 V vs SHE (resp. –0.13 V vs Fc/Fc^+) is independent on the rotation speed and therefore kinetically controlled in contrast to the second wave (0.55 V resp. –0.17 V vs Fc/Fc^+), which is because of its rotation speed dependency diffusion controlled. As expected and displayed in Figure 3, the cyclic voltammogram of the crosslinked polymer **8** as film reveals also two one-electron waves at similar potentials. Rotating disk electrode experiments exhibit in contrast to the non-crosslinked polymer that the intensity of both waves are not dependant on the rotation speed and therefore kinetically controlled (Figure 4). This fact is probably referred to the polymer structure.

Due to the ester functionalization, the polymer is not stable under alkaline conditions; therefore, electrolyte systems at high pH were not investigated.

4. Conclusion

We polymerized a quinone-containing methacrylate monomer in a free-radical polymerization. The influence of the solvent and the initiator concentration on the polymerization were investigated and the electrochemical behavior of this polymer and its crosslinked polymer utilizing cyclic voltammetry and rotation disk electrode experiments. Further work is in progress to explore the application of the polymers as active anode material in organic batteries and air batteries.

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[1] P. Hodge, J. E. Gautrot, *Polym. Int.* **2009**, *58*, 261.
[2] X. Q. Zhu, C. H. Wang, *J. Org. Chem.* **2010**, *75*, 5037.
[3] P. S. Guin, S. Das, P. C. Mandal, *Int. J. Electrochem.* **2012**, 2012.
[4] T. W. Lewis, G. G. Wallace, M. R. Smyth, *Analyst* **1999**, *124*, 213.
[5] K. Naoi, S. Suematsu, A. Manago, *J. Electrochem. Soc.* **2000**, *147*, 420.
[6] K. A. Kun, R. Kunin, *J. Polym. Sci., Part A-1: Poly. Chem.* **1966**, *4*, 859.
[7] T. Janoschka, M. D. Hager, U. S. Schubert, *Adv. Mater.* **2012**, *24*, 6397.
[8] K. Oyaizu, Y. Niibori, A. Takahashi, H. Nishide, *J. Inorg. Organomet. Polym.* **2013**, *23*, 243.
[9] T. Le Gall, K. H. Reiman, M. C. Grossel, J. R. Owen, *J. Power Sources* **2003**, *119*, 316.
[10] T. Yamamoto, T. Kimura, K. Shiraishi, *Macromolecules* **1999**, *32*, 8886.
[11] M. P. Crozet, L. Giraud, J. F. Sabuco, P. Vanelle, M. Barreau, *Tetrahedron Lett.* **1991**, *32*, 4125.
[12] K. Takada, P. Gopalan, C. K. Ober, H. D. Abruna, *Chem. Mater.* **2001**, *13*, 2928.
[13] K. A. Kun, *J. Polym. Sci., Part A: Gen. Pap.* **1965**, *3*, 1833.
[14] K. Oyaizu, W. Choi, H. Nishide, *Polym. Adv. Technol.* **2011**, *22*, 1242.
[15] A. P. Kostikov, V. V. Popik, *J. Org. Chem.* **2007**, *72*, 9190.
[16] T. A. Ayers, R. A. Schnettler, G. Marciniak, K. T. Stewart, R. K. Mishra, D. J. Krysan, B. R. Bernas, P. Bhardwaj, T. L. Fevig, *Tetrahedron: Asymmetry* **1997**, *8*, 45.

Publication P6

P6) “PolyTCAQ in organic batteries: Enhanced capacity at constant cell potential using two-electron-redox-reactions”

B. Häupler, R. Burges, T. Janoschka, T. Jähnert, A. Wild, U. S. Schubert, *J. Mater. Chem. A* **2014**, *2*, 8999–9001.

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PolyTCAQ in organic batteries: enhanced capacity at constant cell potential using two-electron-redox-reactions†

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The application of polymers bearing tetracyano-9,10-anthraquinonedimethane (TCAQ) units as electrode materials in organic batteries enables one narrow charge discharge plateau due to the one two-electron-redox-reaction of the TCAQ core. Li-organic batteries manufactured with this polymer display repeatable charge–discharge characteristics associated with a capacity of 156 mA h g^{-1} and a material activity of 97%.

Polymers with pendant redox-active groups have been employed in different organic electronic devices such as solar cells, organic LEDs and, recently, in organic batteries.[1,2] The utilization of redox-active polymers instead of heavy metals as battery electrodes is highly attractive with regard to recyclability and sustainability.[3] Additionally, polymeric materials for organic batteries have received much attention because of their beneficial properties such as flexibility, lightweight and their cycling performance.[4] A large number of polymers with different redox-active groups have been employed as active material in lithium and/or all organic batteries. From an electrochemical point of view, these polymers can be divided into two main groups, depending on the number of electrons being involved in the electrochemical reaction: (I) a significant number of polymers bear redox-active groups performing only a one-electron-reaction. They mainly consist of persistent organic radicals, like nitroxyls,[5–12] galvinoxyls[13] and redox-active molecules such as carbazoles,[14] triarylamines[15] or phthalimides.[16] Batteries manufactured from these polymers display a privileged charge–discharge behavior with only one plateau, but their theoretical capacity is limited in consequence to their one electron redox process and the molar mass of the repeating unit. For example poly(2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-vinyl ether) (PTVE) features a theoretical capacity of 135 mA h g^{-1},[17] poly(galvinoxylstyrene) of 51 mA h g^{-1} and poly(*N*-vinylcarbazole) as well as poly(triphenylamine) both exhibit a theoretical capacity of 111 mA h g^{-1}. (II) The second group consists of polymers with redox-active groups whose redox reaction involves two or more electrons. These polymers feature higher capacities, but their redox reactions are dependent on each other and, therefore, can occur at different potentials, often leading to one broad respectivly (resp.) multiple charge–discharge plateaus. This behavior is adverse in electric devices that ask for a stable cell-voltage. Polymers bearing carbonyl compounds,[18] poly(imides)[16] or tailor-made radicals are examples for the second group of polymers.[10,19] For instance, polymer-bound pyrene-4,5,9,10-tetraone features a high theoretical capacity of 263 mA h g^{-1}, but the charge–discharge plateau is spread over 1.5 V.[20] Exceptions are polymers with pendant anthraquinone groups like poly(2-vinylanthraquinone).[21] The redox reaction of the anthraquinone occurs in a two-electron-wave.

To provide an alternative to overcome these shortcomings we designed poly(2-vinyl-11,11,12,12-tetracyano-9,10-anthraquinonedimethane) (polyTCAQ) as novel redox-active polymer bearing TCAQs units as pendant groups.[22] These redox-active units feature, due to their special molecular design, one reversible two-electron-redox-reaction.[23] Combining this electrochemical feature with the introduction of a low molar mass polymerizable vinyl group into the TCAQ system, a new monomer with a theoretical charge–discharge capacity of 160 mA h g^{-1} and one charge–discharge plateau was created.

Monomer **4** was obtained in a straightforward three step synthesis (Scheme 1). The amino group of commercially available 2-aminoanthraquinone **1** was transformed into 2-bromoanthraquinone **2** applying a modified Sandmeyer reaction.[24] The vinyl group was introduced by the application of the Hiyama reaction in excellent yields applying Pd(dba)$_2$ as palladium source and JohnPhos as ligand. The carbonyl functionalities of the 2-vinylanthraquinone **3**[25] were transformed to dicyanomethane groups under Knoevenagel conditions to yield monomer **4**.

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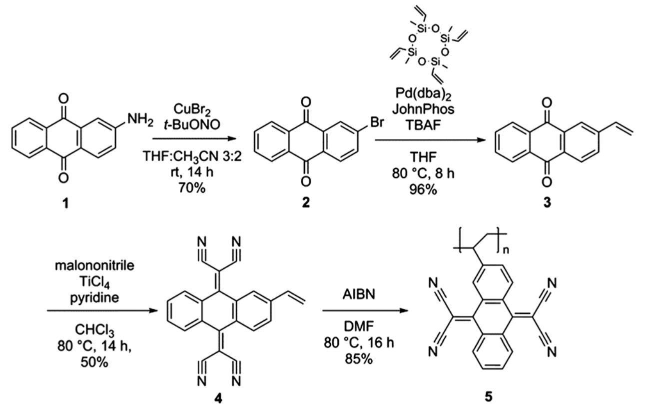
† Electronic supplementary information (ESI) available: Experimental details, size exclusion chromatograms, cyclic voltammograms. See DOI: 10.1039/c4ta01138d



Scheme 1 Schematic representation of the synthesis of polyTCAQ **5**.

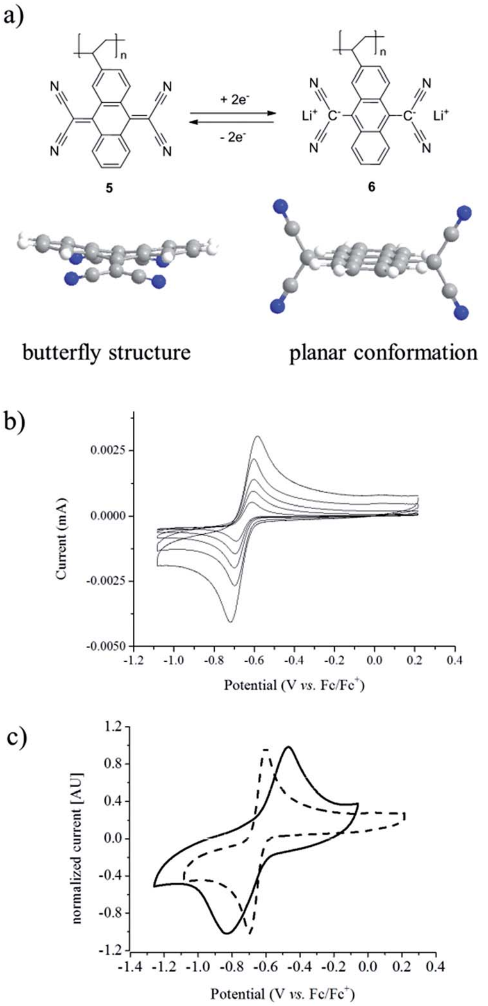


Fig. 1 (a) Schematic representation of the redox couple of polyTCAQ (**5**). (b) Cyclic voltammogram of monomer **4** in propylene carbonate, 0.1 M lithium perchlorate at different scan rates (10, 25, 50, 100 and 250 mV s^{-1}, respectively). (c) Normalized cyclic voltammograms of the monomer **4** in solution (dashed line) and a polymer-composite electrode (solid line) (10/80/10 wt% **5**/VGCF/PVdF) in propylene carbonate, 0.1 M lithium perchlorate.

PolyTCAQ **5** with a molar mass of $M_n = 26\,400$ g mol^{-1} ($M_w/M_n = 1.87$) was prepared by free radical polymerization when the molar mass can be adjusted by the choice of the appropriate solvent. AIBN was used as initiator and DMF as solvent.

The solubility of polymers in an electrolyte is, besides the redox behavior, one of the decisive factors for their application as active electrode material in organic batteries. Too short polymer chains may dissolve in the electrolyte either in the charged or the discharged state and, thereby, lead to capacity loss. In consequence of the low monomer solubility in a large range of common solvents, the polymerization in benzene, toluene or THF lead either to precipitation of the polymer and/or to low yields (see ESI†). Polymer **5** obtained from polymerization with DMF as solvent is soluble in *N*-methylpyrrolidone and insoluble in propylene carbonate. A cyclic voltammogram obtained for monomer **4** in propylene carbonate solution features only one reversible redox wave. As shown in Fig. 1a the expected two one-electron-redox-reactions coincide as one two-electron-redox-reaction, because the structure of the radical anion is twisted and therefore destabilized. The gain of the second electron leads to rearomatization and a planar structure. Hence, the redox potential of the first reduction is lower and both reductions occur at the same potential.[23] Monomer **4** exhibits one two-electron redox reaction wave at −0.64 V *vs.* Fc/Fc$^+$ (Fig. 1b), which is in good agreement with published literature derivates (−0.58 V).[26]

Since most redox-active polymers feature low intrinsic conductivities, the electrochemical behavior of polymer **5** was investigated as composite layer with carbon nanofibers (VGCF) as conducting and polyvinyldene fluoride (PVdF) as binding additive. This composite electrode was prepared by adding a solution of polymer **5** in NMP (10 mg mL^{-1}) to the additives (10/80/10 wt% **5**/VGCF/PVdF). The resulting slurry was mixed, spread onto graphite foil and dried under vacuum. A cyclic voltammogram obtained from these electrodes displayed a reduction at −0.83 V and reoxidation at −0.47 V *vs.* Fc/Fc$^+$ (Fig. 1c). The redox behavior is in good agreement with that of monomer **4** indicating that the polymer backbone does not influence the redox behavior. The small shift compared to the values of **4** is caused by hindered kinetics due to the high viscosity of propylene carbonate and the thickness of the electrode. Importantly, the intensities of the oxidation and the reduction peaks are constant for over 100 cycles (see ESI†), indicating the stability of the polymer in the electrolyte (Fig. 1c).

A coin type cell battery was manufactured under inert atmosphere with a lithium metal anode and the polymer composite electrode (20/40/30/10 wt% **5**/Super P®/VGCF/PVdF) as cathode. A 0.1 M solution of lithium perchlorate in propylene carbonate served as electrolyte. The battery exhibits a highly reversible charge–discharge behavior featuring an average cell voltage of 3.05 V for charging and 2.25 V for discharging *vs.* Li/Li$^+$ (Fig. 2). This behavior is consistent with the redox waves observed in the cyclic voltammogram of the electrode. The cell was charged and discharged at a charging speed of 1 C. The rate of *n* C corresponds to a full charge–discharge in 1/*n* hours. After the 1st cycle a material activity of 97% resp. 156 mA h g^{-1} was observed (Fig. 3). The prototype device features a good cyclability: after 500 charge–discharge cycles, the battery maintains

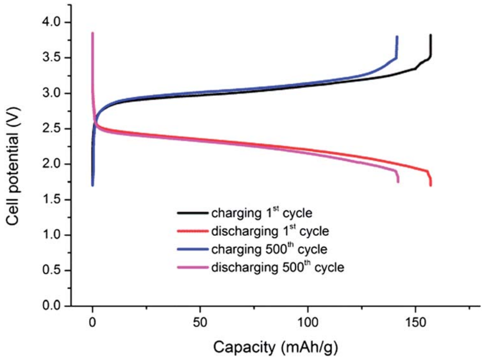


Fig. 2 Charge–discharging curves (capacity *vs.* potential) of the Li-organic battery of the 1st and the 500th cycle. The anode is lithium metal, the cathode is a composite with polyTCAQ **5** as active material.

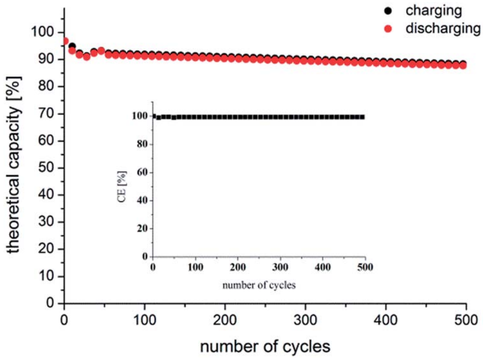


Fig. 3 Extended charge–discharge cycling of **5** in propylene carbonate, 0.1 M lithium perchlorate (500 cycles, 1 C). Coulombic efficiency (CE%) of 500 charge–discharge cycles (black squares).

88% of the initial capacity (141 mA h g^{-1}) at a consistently high coulombic efficiency of 99%. Coin type cells with a larger amount of active material like 30 wt% led to lower material activity of 68% (see Fig. S2†).

Conclusions

In conclusion, tetracyano-9,10-anthraquinonedimethanes (TCAQ) represent promising core structures for active electrode materials in organic batteries. Their interesting redox behavior consisting of one two-electron-reduction/oxidation-wave leads to one charge–discharge plateau associated with a good charge storage capacity. To maintain the theoretical capacity of the polymer as high as possible, polyTCAQ **5** was synthesized within four straightforward steps. Comparison of the cyclic voltammograms of the monomer in solution and the polymer as composite electrode indicate that, both, the polymer backbone and the conducting and binding additives have no influence on the redox behavior. A Li-organic prototype battery applying polyTCAQ as active electrode material displays a high material activity of 97%, high rechargability of 500 cycles with 12% loss, as well as excellent coulombic efficiency (99%), which shows that polyTCAQ represents an interesting candidate as active electrode material in organic batteries.

Notes and references

1 Y. L. Liang, Z. L. Tao and J. Chen, *Adv. Energy Mater.*, 2012, **2**, 742.
2 T. Janoschka, M. D. Hager and U. S. Schubert, *Adv. Mater.*, 2012, **24**, 6397.
3 P. Poizot and F. Dolhem, *Energy Environ. Sci.*, 2011, **4**, 2003.
4 H. Nishide and K. Oyaizu, *Science*, 2008, **319**, 737.
5 K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, J. Iriyama, M. Suguro and E. Hasegawa, *Chem. Phys. Lett.*, 2002, **359**, 351.
6 K. Nakahara, J. Iriyama, S. Iwasa, M. Suguro, M. Satoh and E. J. Cairns, *J. Power Sources*, 2007, **165**, 870.
7 M. Suguro, S. Iwasa, Y. Kusachi, Y. Morioka and K. Nakahara, *Macromol. Rapid Commun.*, 2007, **28**, 1929.
8 K. Oyaizu, T. Kawamoto, T. Suga and H. Nishide, *Macromolecules*, 2010, **43**, 10382.
9 J. Qu, T. Katsumata, M. Satoh, J. Wada, J. Igarashi, K. Mizoguchi and T. Masuda, *Chem. – Eur. J.*, 2007, **13**, 7965.
10 J. Q. Qu, T. Katsumata, M. Satoh, J. Wada and T. Masuda, *Macromolecules*, 2007, **40**, 3136.
11 T. Katsumata, J. Q. Qu, M. Shiotsuki, M. Satoh, J. Wada, J. Igarashi, K. Mizoguchi and T. Masuda, *Macromolecules*, 2008, **41**, 1175.
12 T. Katsumata, M. Satoh, J. Wada, M. Shiotsuki, F. Sanda and T. Masuda, *Macromol. Rapid Commun.*, 2006, **27**, 1206.
13 T. Suga, H. Ohshiro, S. Sugita, K. Oyaizu and H. Nishide, *Adv. Mater.*, 2009, **21**, 1627.
14 M. Yao, H. Senoh, T. Sakai and T. Kiyobayashi, *J. Power Sources*, 2012, **202**, 364.
15 J. K. Feng, Y. L. Cao, X. P. Ai and H. X. Yang, *J. Power Sources*, 2008, **177**, 199.
16 K. Oyaizu, A. Hatemata, W. Choi and H. Nishide, *J. Mater. Chem.*, 2010, **20**, 5404.
17 M. Suguro, S. Iwasa and K. Nakahara, *Macromol. Rapid Commun.*, 2008, **29**, 1635.
18 Z. P. Song, H. Zhan and Y. H. Zhou, *Chem. Commun.*, 2009, 448.
19 P. Nesvadba, L. Bugnon, P. Maire and P. Novak, *Chem. Mater.*, 2010, **22**, 783.
20 T. Nokami, T. Matsuo, Y. Inatomi, N. Hojo, T. Tsukagoshi, H. Yoshizawa, A. Shimizu, H. Kuramoto, K. Komae, H. Tsuyama and J. Yoshida, *J. Am. Chem. Soc.*, 2012, **134**, 19694.
21 W. Choi, D. Harada, K. Oyaizu and H. Nishide, *J. Am. Chem. Soc.*, 2011, **133**, 19839.
22 R. Gomez, C. Seoane and J. L. Segura, *Chem. Soc. Rev.*, 2007, **36**, 1305.
23 A. M. Kini, D. O. Cowan, F. Gerson and R. Mockel, *J. Am. Chem. Soc.*, 1985, **107**, 556.
24 N. Seidel, T. Hahn, S. Liebing, W. Seichter, J. Kortus and E. Weber, *New J. Chem.*, 2013, **37**, 601.
25 M. C. Diaz, B. M. Illescas, C. Seoane and N. Martin, *J. Org. Chem.*, 2004, **69**, 4492.
26 M. A. Herranz, B. Illescas, N. Martin, C. P. Luo and D. M. Guldi, *J. Org. Chem.*, 2000, **65**, 5728.

Publication P7

P7) “Application of phenolic radicals for antioxidants, as active materials in batteries, magnetic materials and ligands for metal-complexes”

T. Jähnert, M. D. Hager, U. S. Schubert, *J. Mater. Chem. A* **2014***, **2***, 15234–15251.

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Application of phenolic radicals for antioxidants, as active materials in batteries, magnetic materials and ligands for metal-complexes

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Organic radicals originating from phenolic compounds have been known for decades. The most well-known of these radical species are the phenoxyl-radical and the galvinoxyl-radical. Those radicals are characterized by the unpaired electron at a formerly phenolic oxygen-atom. In natural systems phenolic radicals are often found as intermediate products or as part of antioxidant and radical-scavenging processes. Tyrosyl-radicals or tocopherol-radicals represent typical examples. More reactive radicals like the hydroxyl-radical come in contact with these compounds and react to harmless water, while the radical is passed to the phenolic compound. Other radical scavengers in biological systems are, *e.g.*, flavonoid molecules like catechin, luteolin and quercetin as well as resveratrol, vanillin or neurotransmitters like dopamine and epinephrine. In organic radical batteries phenoxyl-radicals or galvinoxyl-radicals can play a pivotal role as electroactive material to store electric energy. They are also often investigated for their magnetic properties, or their redox-activity when used in metal-complexes. From the tyrosyl-radical as part of enzymes to galvinoxyl as dopant in organic solar cells phenolic radicals display great versatility in structure and function. This review summarizes the application of phenol-based radicals in biological as well as artificial materials and systems over the last years.

Introduction

Every phenolic compound can be oxidized to its radical form, *i.e.* compounds with an unpaired electron. While most of these species are highly reactive and have short lifetimes,[1,2] there are also some radicals, which are stable for days or even years. Their stability is strongly dependent on the substitution-pattern. Many phenolic radicals can be found in plants, animals and even humans.[3,4] They can be present in their radical-form or be part of a reaction mechanism.[5,6] Phenolic compounds found in organic life can act as radical scavengers and antioxidants, *e.g.*, vitamin E, tocopherol. By donating a hydrogen radical it can be converted to its radical form. Many phenols or polyphenols like flavonoids,[7] catechins[8] as well as resveratrol[9–11] and vanillin[12] react in this way. It has been discovered that many neurotransmitters also act as antioxidants, because of the large amount of reactive oxygen species the brain is exposed to.[13] It is also believed that these radicals are partly the cause for schizophrenia. Resveratrol, another prominent phenolic compound found in wine and grapes, can prevent inflammation, atherosclerosis and carcinogenesis.[11] This function is due to resveratrols ability to purge free radicals. On the other hand resveratrol can enhance the radiosensitivity of cancer cell-lines to radiative treatment, while protecting normal tissue from oxidative stress.[10] One of the most prominent ways to determine such antioxidant activity is the reaction with galvinoxyl- or phenoxyl-radicals. These radicals have been known in recent days for their use in organic radical batteries (ORB),[14] for magnetic applications[15] or in solar-cells (Fig. 1).[16]

Apart from resveratrol grapes also contain a variety of other compounds with antioxidant ability. Carotenoids are noteworthy in this context, because by acting as antioxidants, they also prevent age-related macular degeneration against UV-radiation.[2] Another potent antioxidant is vanillin. Its antimutagenic properties were first described in 1986 and since then it has been discovered that vanillin can significantly reduce mutations induced by ultraviolet light or X-rays.[12]

In other biological systems phenoxyl radicals play an important role as part of metallo-complexes in enzymes.[17–20] As one of the most important amino-acid radicals[21] the tyrosyl-radical is found in proteins, where it acts as cofactor to promote oxidation reactions. In enzymes like galactose oxidase[17,19] it is coordinated to a copper ion, which is located in the protein active site.[22] The tyrosyl-radical has also been characterized in a number of Zn(II), Ni(II) or Co(III) metal complexes.[23] Zn–phenoxyl-complexes are also used to model the spectroscopic, redox and structural properties of their Cu-counterparts.[18] As an

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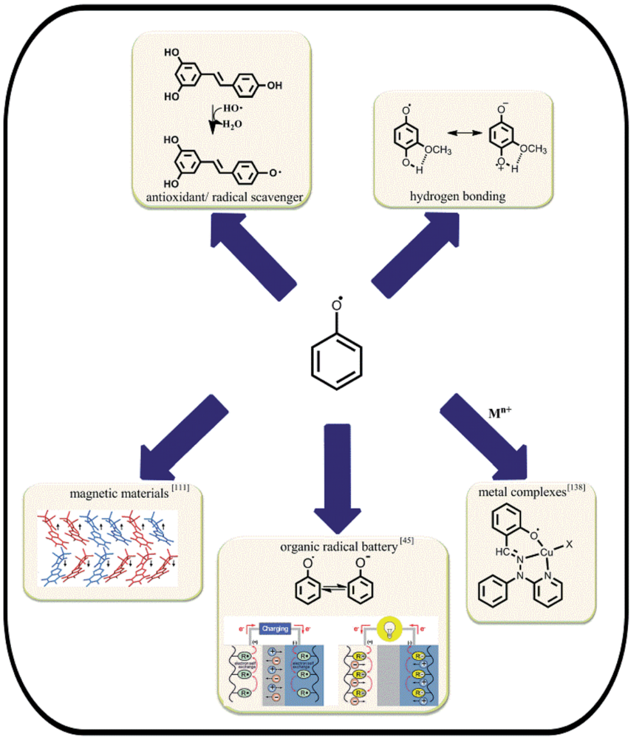
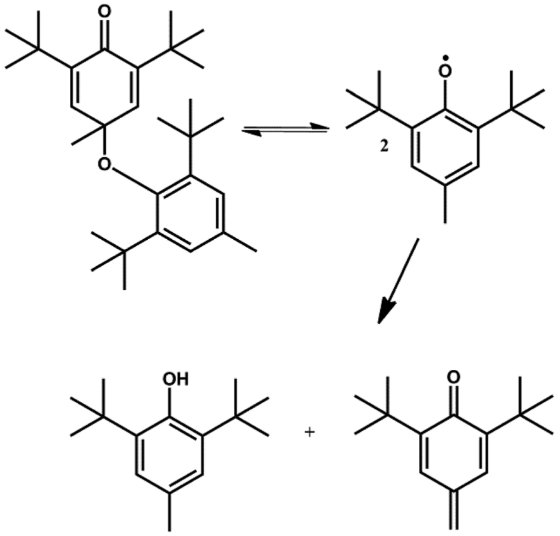


Fig. 1 Uses of phenolic radicals as antioxidant/radical scavenger, for hydrogen bonding, magnetic materials, organic radical batteries and in metal complexes (included figures reprinted with permission from ref. 45 and ref. 111).

Fe(III)-centered enzyme ribonucleotide reductase catalyzes DNA synthesis by reducing ribonucleotides. The catalytic process of this enzyme involves the formation of a tyrosyl-radical close to the iron-center, which also proves the importance of this radical in biological systems.[21]

The synthesis of new phenoxyl-radicals was, for a long time, driven by the desire to create new magnetic materials or molecules with half-metal characteristics. Phenoxyl-radicals used for their magnetic properties need to be sufficiently stable and usually possess bulky substituents like *t*-butyl in *ortho*-position.[24,25] The *para*-position is open to the creativity of the chemist and can be functionalized with almost every substituent that stabilizes the radical.[26] Apart from substituents like hydrogen or methyl, which open pathways for dimerization and other side-reactions (Scheme 1), many substituents can be used to create stable free radicals.[27] For all molecular magnets a prediction of their properties at the microscopic level is rather difficult and understanding the spin–spin interactions of the molecule is the key to comprehend the magnetic properties.[28] For this purpose a theoretical understanding is required as well as chemical expertise. Recent quantum chemical calculations described the magnetic properties of molecular magnetic materials using state-of-the-art theoretical calculations.[29] Tyrosyl-radicals have also been investigated for their magnetic properties, but the most prominent radical for molecular magnets is the galvinoxyl-radical, with its unparalleled stability.[24] To investigate spin-concentration and magnetic properties galvinoxyl-radicals connected to conjugated polymers have been synthesized and tested.[15,30]



Scheme 1 Schematic representation of the dimerization or dissociation of the 2,6-di-*t*-butyl-4-methylphenoxyl radical.

After the first publication on the topic of organic radical batteries (ORBs) many of the radical-polymers developed for use as magnetic materials were re-evaluated as electrode materials. Polymeric materials containing galvinoxyl-radicals were used as anode-active materials for ORBs with varying success. Styrene-polymers with galvinoxyl side-chains have been used in conjunction with several other redox-active polymers[31–33] to form metal-free, environmentally benign ORBs and the future holds much more in stock for this field of research.

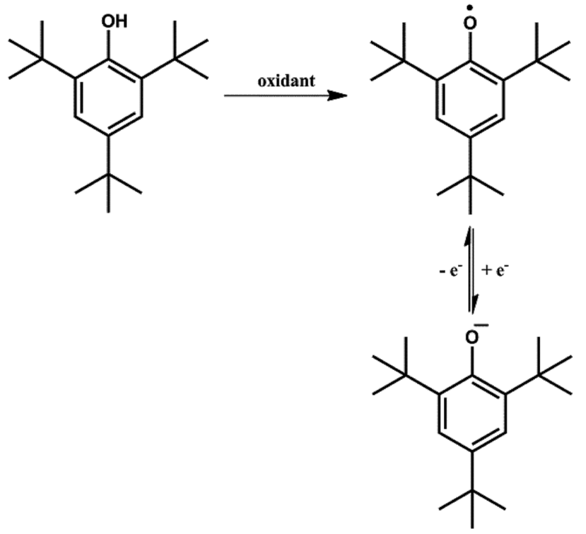
Other fields of use for phenolic radicals, like hydrogen-bonding studies,[34] are much less prominent than the previously named, but play their role regarding the stability and reactivity of phenolic radicals.

Theoretical considerations

Stability and redox-chemistry of phenolic radicals

Phenolic radicals, as well as all other radicals, possess an unpaired electron. In phenolic radicals this electron is delocalized over the aromatic ring and its substituents.[27] The high reactivity of these systems can be diminished by introducing bulky substituents in the *ortho*- and *para*-positions.[26] One of the most stable phenoxyl-radicals, which is used as experimental standard, is the 2,4,6-tri-*t*-butylphenoxyl radical (Scheme 2).[27]

The three bulky *tert*-butyl moieties serve to hinder pathways that lead to dimerization, disproportionation, hydrogen abstraction or addition-reactions (Scheme 1).[26] The generation of such phenolic radicals is easily achieved by chemical oxidation with PbO_2 or $K_3[Fe(CN)_6]$,[14,35] laser photolysis,[36] which occurred along the photo-excited S_1-state and not the triplet-state, as well as oxidation with highly reactive radicals like the hydroxyl-radical.[37] In this context the phenol acts as radical scavenger. The antioxidant strength of a phenol-derivative is correlated to the corresponding phenoxyl-radicals stability and evaluated by the phenolic OH-bond dissociation enthalpy.[38]

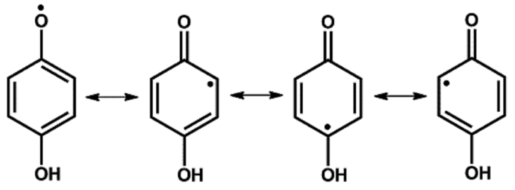


Scheme 2 Schematic representation of the oxidation and following redox activity of 2,4,6-tri-*t*-butylphenoxyl and its radical.

Calculations and experimental measurements have shown, that bond dissociation enthalpies between ~327 kJ mol^{-1} for tocopherol and other highly substituted phenols and ~368 kJ mol^{-1} for unsubstituted phenol can be found, showing the importance of the number and nature of the substituents.[39] Antioxidant activity of phenols in biological systems is almost always a result of the creation of highly reactive free radicals by ionizing radiation. Generated radicals can range from hydroxyl-, peroxide- and azide-radicals to oxide radical anions, which all lead to the generation of phenoxyl-radicals.[40] Theoretical studies have shown that thermal decomposition by elimination of carbon monoxide to cyclopentadienyl requires activation-energies of ~230 kJ mol^{-1} and addition of oxygen would also be highly endothermic, negating these reactions as decomposition-ways under ambient conditions.

In most cases in biological systems the formed phenoxyl-radical dimerizes shortly after its generation unless its substitution-pattern stabilizes the radical.[41] When phenoxyl-radicals possess conjugated heterocyclic rings as substituents in *para*-position the spin-density of the whole molecule can be delocalized, hereby the major spin-density is moved away from the phenoxyl-radical (Scheme 3).

This strategy can be used to tune the spin-density for applications in molecular based magnetic materials.[24,42] The phenoxyl-radical has been investigated over a long period of time, experimentally and theoretically, including vibrational spectroscopy, ESR spectroscopy and electrochemistry.[43] Phenolic radicals, stabilized with bulky substituents, can also be reduced to their anionic form and reoxidized to the radical indefinitely. Most of these phenoxyl radicals possess relatively low redox-potentials (~0 V *vs.* Ag/AgCl or less).[44,45]



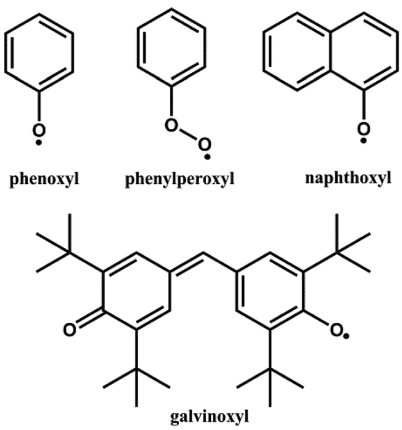
Scheme 3 Schematic representation of the delocalization of the radical in the *p*-hydroxyphenoxyl radical system.

Important phenolic radicals – basic structures

Most phenolic radicals are based on the phenoxyl-radical. The term 'phenoxyl-radical' is also often used as synonym for all phenolic radicals (Scheme 4).[26] The variety of different radicals embraces the basic phenoxyl,[43] which can be obtained by oxidation from phenol, and other substituted phenoxyls.[39] Phenoxyl-radicals have been investigated as organic molecules,[46] as well as side chains of polymers.[47–50] On the molecular level, the investigations are often focused on the formation of the radicals, the underlying reaction mechanism[46] as well as the influence of substituents during formation and on the stability.[51] Many of the structurally hindered phenoxyl-radicals have been subject to electron spin resonance (ESR) studies and stability examinations to determine their long-time stability under different temperatures and environments.[52] In related studies phenoxyl-radicals were incorporated in a corannulene to create a curved π-conjugated molecule. As neutral radical phenoxyl proved to be a useful probe for studying intramolecular magnetic interactions in organic molecules.[53]

The radical formation was also investigated in polymers containing phenoxyls. These polymers have been created by UV-photolysis of lignin-polymers.[54] Additionally conjugated polymers, like polythiophene[50] and poly(isonaphthene methine),[47] bearing phenoxyl-moieties have also gained interest due to their low band-gap value,[47] high spin-concentration and magnetic properties.[50] Styrene-based polymers containing phenoxyl-groups have also been successfully synthesized and evaluated for their magnetic properties.[49] These polymers can vary from linear or star-shaped to highly branched architectures.[48]

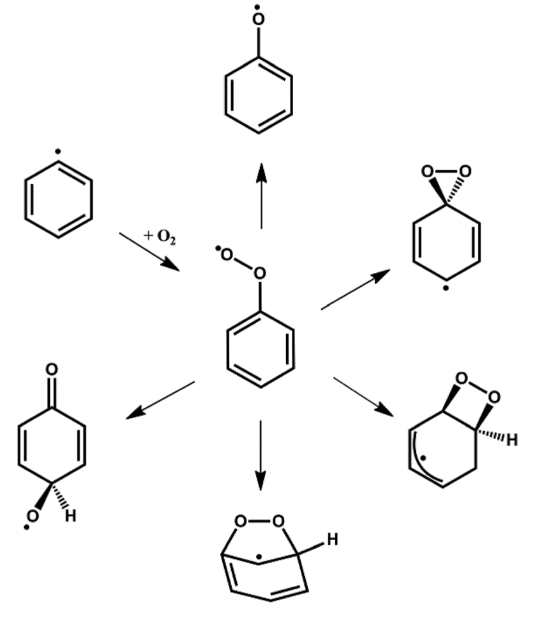
Another phenolic radical is the phenylperoxyl-radical, which can arise from phenyl radicals by reaction with oxygen. Those



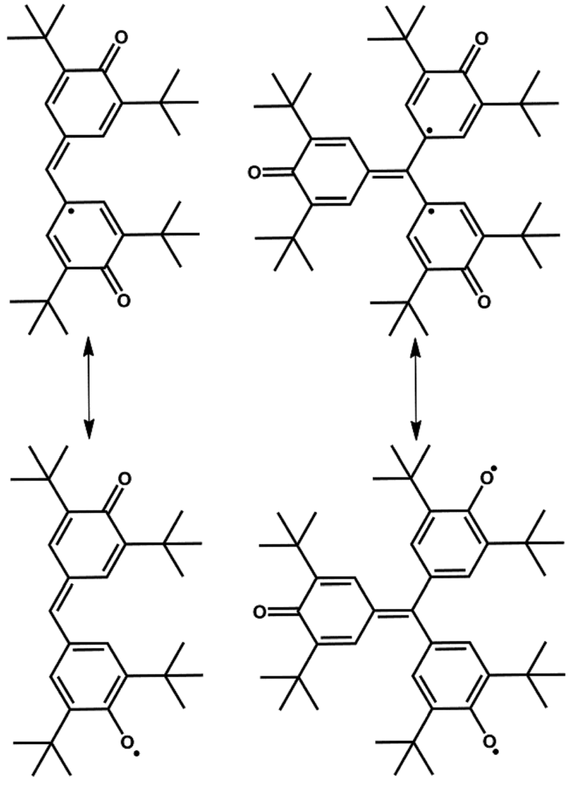
Scheme 4 Schematic representation of selected phenolic radical structures.

simple radicals can decompose to phenoxyl-radicals or cyclopentadienyl-radicals (Scheme 5).[55,56]

Peroxyl-radicals are important in combustion-processes, oxidation of volatile organic compounds in the atmosphere and also play a role in cellular lipid oxidation and DNA damage.[57] The study of phenylperoxyl-radicals is largely focused on their generation,[55] subsequent reactions[57] and decay of these radicals.[58] Phenylperoxyl-radicals formed by reaction of phenyl-radical and oxygen contribute to ozone formation during combustion of aromatic hydrocarbons.[59] Furthermore, the phenylperoxyl radical is believed to be the primary intermediate of all degradation-products of aromatic hydrocarbons, which are formed during combustion.[60,61] The reactivity of these radicals is also influenced by substituents. Electron-withdrawing substituents in *para*-position to the radical increase the rate-constant for oxidation by the radical, while electron-donating decrease it.[62] Peroxyl-radicals can also be generated through reaction of a naphthyl-radical with oxygen. The resulting naphthyl–peroxyl radical can decompose in a number of ways, one leading to the formation of naphthoxy-radicals.[63] Naphthoxyl-radicals have gained only low significance in literature, because most applications or measurements were performed with their smaller counterparts. The main research focus is in health, because naphthoxyl-radicals are intermediates in the dissociation of nitrated aromatic hydrocarbons, which can be emitted through combustion processes and can be carcinogenic and mutagenic.[64,65] The most unique and probably the most investigated phenolic radical is the galvinoxyl-radical. This radical deserves special attention due to the excellent stability, almost complete inertness against oxygen and its structure, which is similar to that of triphenylmethyl-radicals, but as a delocalized allyl-type radical.[26] Although most galvinoxyls possess only a single radical site, a diradical also exists, which can illuminate the electronical structure more accurately.[66] Investigations of this diradical revealed that most of the spin-density of the molecule is located on the carbons adjacent to the center carbon-atom similar to Yang's biradical (Scheme 6).[26]



Scheme 5 Schematic representation of decomposition-paths of the phenylperoxyl-radical (redrawn according to ref. 61).



Scheme 6 Schematic representation of the resonance-structures of the galvinoxyl-radical (left) and Yang's biradical (right) (redrawn in accordance to ref. 26).

The stability of the radical stems from this delocalization of the unpaired electron as well as the bulky *tert*-butyl substituents, which cause steric hindrance.[67] Galvinoxyl, similar to other phenoxyl-radicals, can be reversibly reduced to its anionic form enabling the utilization in energy-storage applications.[14,44,45] Incorporation of galvinoxyl-moieties into polymers was mostly achieved by side-chain moieties. Most of the unconjugated galvinoxyl-polymers are styrene-polymers.[35,44] Conjugated polymers with galvinoxyl-groups were synthesized with different backbones, such as polythiophenes[30] or phenyl-ethylene coupled polymers.[68,69] As well as binaphthyl-spacers and represent interesting research objects because of their optical activity and magnetic properties.[70]

Important phenolic radicals – radical scavengers and antioxidants

Many reactive oxygen species and free radicals are involved in pathological conditions like cancer or aging. The excess of reactive oxygen species generated by ionizing radiation or cellular respiration can be diminished and contained by antioxidants found in many fruits.[10] Such antioxidants like resveratrol can have beneficial effects on those conditions.[5]

Before further examples are given, a brief definition of antioxidant activity and radical scavenging ability has to be given: Antioxidant activity characterizes the ability of a compound to hinder an oxidation process, while radical scavenging describes the ability to react with free radicals.[6] These processes can be separate, but in some cases can also be one and the same, *e.g.*, the scavenging of hydroxyl-radicals by resveratrol to prevent oxidative damage to biological systems.[9] Because this review is focusing on phenolic radicals, radical scavenging ability and antioxidative activity will not be handled separately.

Phenolic compounds are widely distributed in plants and display an important class of antioxidants (Fig. 2).[71] Resveratrol is one of the most studied phenolic antioxidants. Great effort has been put into the development of antioxidants more effective than resveratrol.[72] Because of this significant interest, it is important to go into detail about resveratrol and its abilities. The radical scavenging ability of resveratrol allows it to react with free radicals, which would otherwise cause tissue-damage and can lead to several diseases.[10] Apart from radical scavenging resveratrol also suppresses lipid peroxidation by chelation of copper(II).[11] The efficiency of radical-scavenging is corresponding to the bond-dissociation-enthalpy of the hydroxyl-group. By elongating the alkyl-chain between the phenols in resveratrol the bond-dissociation-enthalpy of the 4-OH decreases, resulting in larger radical-scavenging activity.[9] Stilbene-analogues to resveratrol like 4,4′-dihydroxy-*trans*-stilbene,[73] 3,5-dihydroxy-*trans*-stilbene or 3,4-dihydroxy-*trans*-stilbene[74] have been investigated for their radical scavenging capacity. 4,4′-Dihydroxy-*trans*-stilbene exhibits higher radical scavenging activity than resveratrol and shows the importance of the 4′-OH.[73] Still 3,4-dihydroxy-*trans*-stilbene possesses an even stronger antioxidative effect. Substitutions on one hydroxide of 4,4′-dihydroxy-*trans*-stilbene are also influencing this behavior. Electron-withdrawing groups diminish the radical-scavenging activity while electron-donors increase it.[74] The substitution of the OH-group for an SH-group also improves the performance in contrast to resveratrol. Some mercaptostilbenes are 10^4-times more active than resveratrol.[72] All of the hydroxyl-substituted Schiff bases can be obtained from the reaction of the corresponding aldehyde and aniline and possess radical-scavenging activity similar to that of resveratrol.[75] It has also been discovered that the number of hydroxyl-groups in the molecule also increases the scavenging activity. In this context resveratrol is less active than piceatannol, which possesses one more hydroxyl-group.[76] All these radical scavengers are oxidized to their radical form during the scavenging process, which does not become a problem in itself, because these radicals decompose harmlessly.

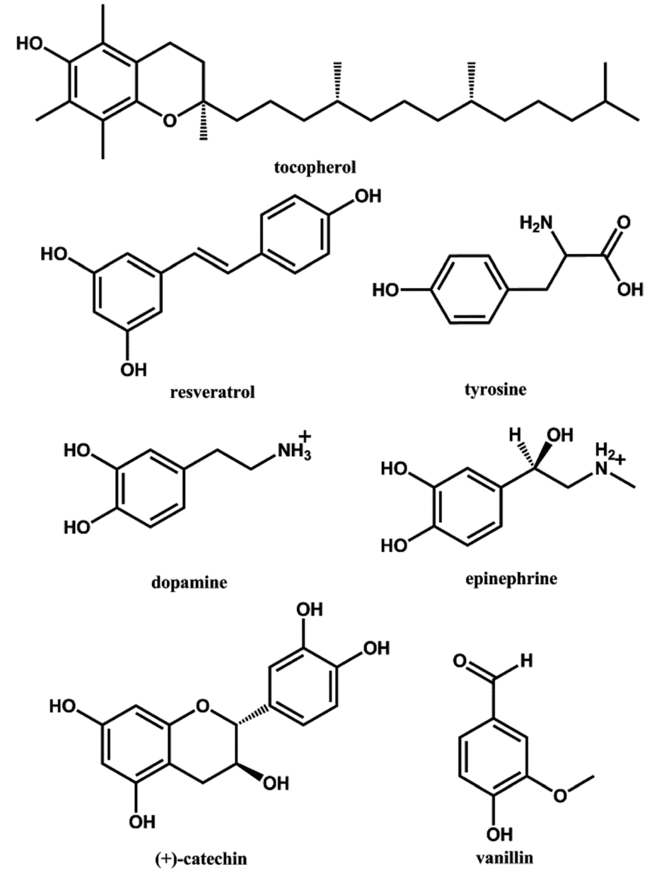
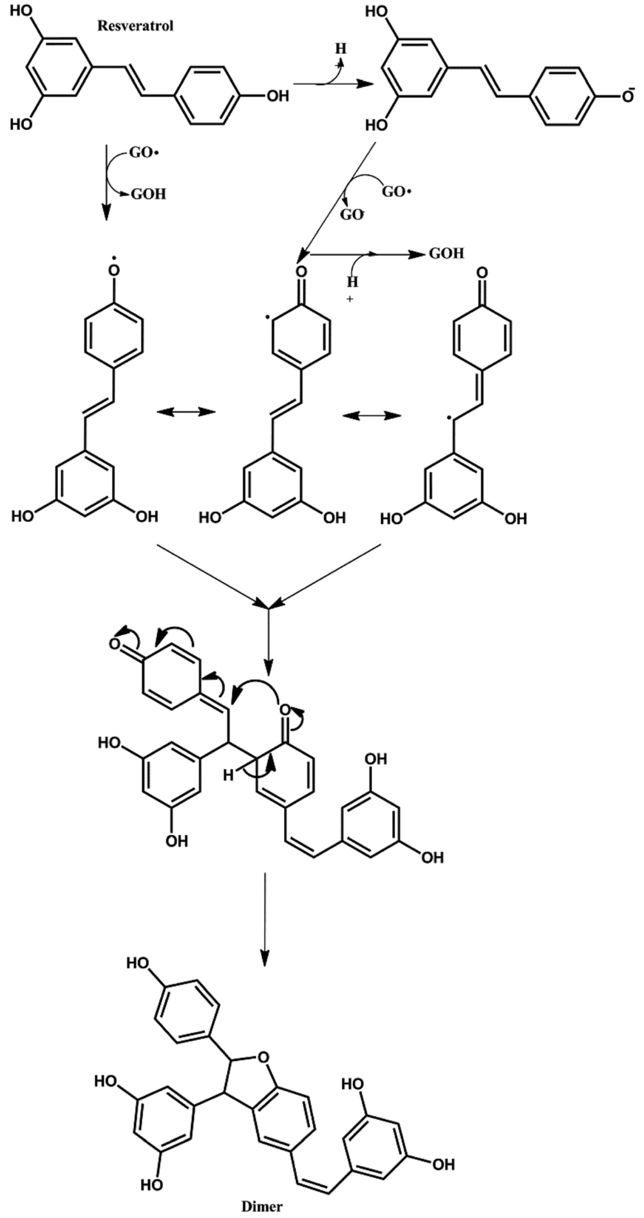


Fig. 2 Schematic representation of phenolic antioxidants I.

The major decomposition pathway for these radicals is the dimerization. In case of resveratrol, a dihydrofuran-dimer and in case of 4,4′-dihydroxy-*trans*-stilbene a dioxane-dimer is obtained (Scheme 7).[74] Many phenolic substances possess radical scavenging capacity. Among those are salicylate and 4-aminophenol-derivatives, like the common pain-medications acetylsalicylic acid and paracetamol. The study of these derivatives shows that electron-withdrawing groups destabilize the radical, while electron-donors lead to a stabilization.[77] Curcumin and derivatives have also been in the focus of radical scavenging research.

Due to its conjugated structure the corresponding radical is stabilized through resonance stabilization. The radical can be localized at the two phenol-groups and the central CH_2-group.[78,79] The introduction of ferrocene to curcumin has been tested to improve the radical-scavenging capacity, but the presence of ferrocene might mediate the creation of hydroxyl-radicals in the presence of hydrogen peroxide, which makes this concept only applicable in selected cases.[80] A phenolic compound that has been often used as reference for radical scavenging is trolox (Fig. 3).[78] As an analogue to tocopherol it is used for such studies, because of its solubility in polar solvents and stability. Trolox has similar antioxidant-activities as α-tocopherol, but significantly lower than vanillin or vanillic acid.[81] Vitamin E can be defined as eight tocopherols and tocotrienols, which all share a similar structure.[82] α-Tocopherol is the most abundant and biologically active form of vitamin E and also the most studied.[4] Tocopherol plays a large role in tissue cells and acts as antioxidant to prevent living cell membranes from decomposing.[83] The reason for the radical scavenging effectiveness lies in tocopherols ability to generate stable radicals. The two methyl-groups in *ortho*-position to the radical-center are sterically hindering the phenoxyl-radical, increasing its stability.[84]



Scheme 7 Schematic representation of the dimerization-mechanism of resveratrol-radicals (redrawn in accordance to ref. 74).

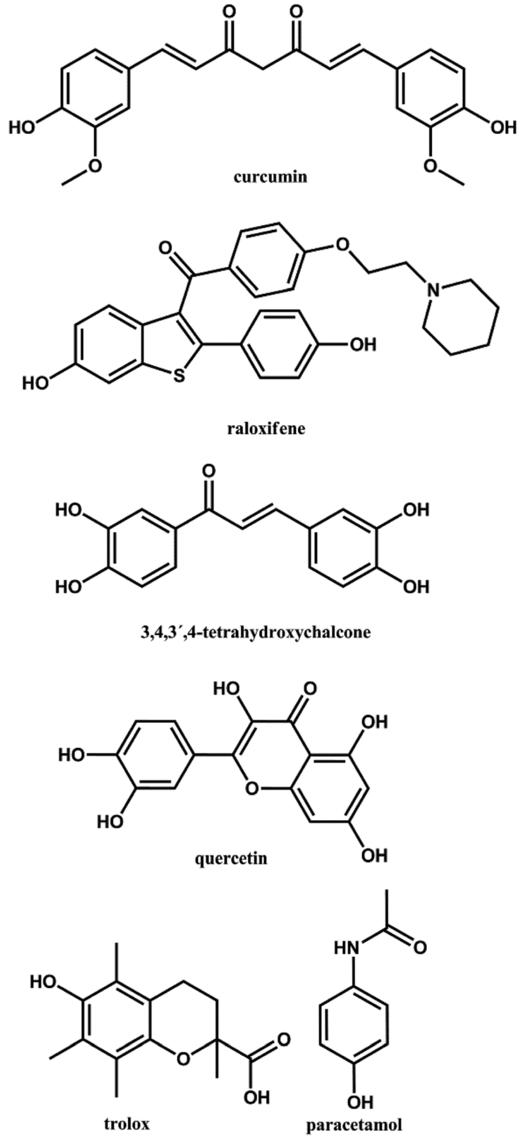


Fig. 3 Schematic representation of phenolic antioxidants II.

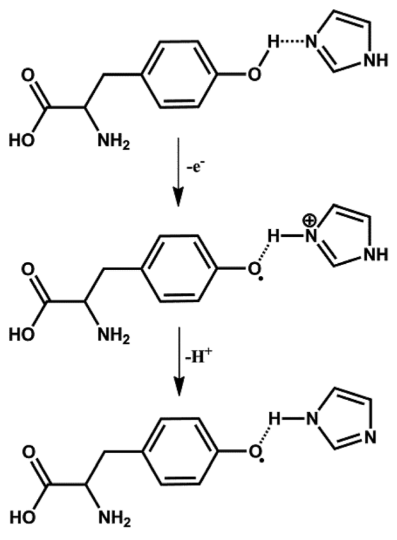
The radical is created by hydrogen-transfer from its OH-group during radical scavenging. The mechanism has not been fully investigated, so there are two possibilities: a one-step hydrogen-transfer or electron transfer with a following proton transfer.[85] Tocopherol may be an effective radical-scavenger,[86] but as antioxidant to hydrogen peroxide it is ineffective[71,87] as well as in retarding the oxidative deterioration of lipids in complex food systems.[88] Many other phenolic compounds have been tested for their radical scavenging capacity. *e.g.*, chalcones,[89] flavonoids,[90] tannins,[91] or even the estrogen-receptor raloxifene (Fig. 3).[92] All of these compounds can undergo oxidation to the corresponding phenoxyl-radical during the process of radical-scavenging or as antioxidant. The resulting radicals vary greatly in stability depending on the substitution-pattern, but all are less harmful than the peroxyl- or hydroxyl-radicals, which are scavenged by these radicals. Phenolic antioxidants are often found in plants like chamomile,[93] *Helianthemum taxa* (Cistaceae),[94] cherimoya,[95] tree bark,[96] apples,[97] or grapes.[2] Many of the healthy attributes of plants or fruits can be attributed to their radical-scavenging ability and their antioxidant character. Most of the tested substances were investigated for their use in biological systems *e.g.* to inhibit the oxidation of polyunsaturated fatty acids[97] or used as dietary supplements[95] and drugs.[94] An investigated scavenging opportunity regarding polymeric compounds is the scavenging of radicals released by polymeric materials in the human body. To polymerize *e.g.* methyl methacrylates for denture-repair resins benzoyl peroxide is used as initiator. Phenols such as (+)-catechin, (−)-epicatechin or curcumin can scavenge radicals generated from traces of this material and prevent inflammation or allergic reactions.[7]

The role of hydrogen-bonding in phenoxyl radicals

Hydrogen bonding is a fundamental form of a non-covalent interaction in many natural and synthetic systems. Hydrogen-bonding is usually observed for closed-shell systems, but also exists for radical moieties.[34] These open-shell hydrogen-bonds are often found in enzymatic systems.[98] Hydrogen-atom transfer reactions also present an important sequence in industrial and natural processes. Oxygen insertion reactions in biological systems by cytochrom P450 is one of such procedures. In model-compounds it was found that phenoxyl-radicals can be part of these systems. In these tests phenolic compounds acted as hydrogen-radical donors, forming the radical as result.[99] In case of tyrosine it has been observed that the synchronous transfer of electrons and protons is more efficient compared to the step-wise processes. The simultaneous mechanism is the dominant one in the oxidation of phenols bearing pendant bases like pyridine.[100] In addition to intermolecular hydrogen-bonding phenoxyl-radicals can also show intramolecular hydrogen-bonding. Benzimidazole-phenoxyl compounds have been synthesized and investigated regarding the proton-coupled electron transfer reaction, which is believed to be the oxidation mechanism of tyrosyl if it is not coupled to a metal ion (Scheme 8).[101]

Inter- and intramolecular hydrogen-bonds not involving the reactive positions can modulate the rate of H-abstraction by stabilizing or destabilizing the radical.[102] Intermolecular hydrogen-bonding between phenols and solvent molecule acceptors have been known to reduce the ability to donate hydrogen-radicals to other radicals. In contrast to that are 1,2-diols of acrylic origin. This is because the oxygen-radical in these systems is a much better hydrogen-bond acceptor than the hydroxyl-group it substitutes.[103] With *ortho*-substituted amide-phenoxyls the influence of H-bonding on the properties of the phenoxyl/phenolate redox-couple was investigated. This study revealed that the presence of hydrogen-bonding does not hinder redox-reactions of the radical, but that the redox-potential is influenced by it. This influence can lead to differences in the redox-potential of several hundred millivolts between H-bonded and non-H-bonded compounds (Fig. 4).[104]

The concept for H-bonding with radicals is comparable to that of closed-shell complexes, meaning that it follows a n → σ* donor–acceptor mechanism, but a radical-induced charge-shift can modulate the strength of these interactions. This can help to identify new radical species with unique properties.[105] The electrochemical properties of phenoxyls can also be modulated by intermolecular hydrogen-bonding. The strength of the hydrogen-bond partner and its deviation from planarity are factors that influence these changes.[101,106] In the process of radical scavenging radicals are abstracted, often by phenoxyl-radicals, from more reactive radical-molecules. Radicals can also abstract hydrogen-radicals from closed-shell compounds and leave the corresponding radical as result. It was discovered that the rate for hydrogen abstraction decreases with the increase in solvent hydrogen bond acceptor ability.[107] This means the stronger the radical is hydrogen-bonded, the less likely it is to abstract hydrogen from other molecules. Hydrogen-abstraction like this represents an important process for many enzymatic reactions. One of the most prominent examples is galactose oxidase, in which a tyrosyl-radical is coordinated to copper(II).[108] The tyrosyl-radical is also part of the ribonucleotide reductase, which catalyses the reduction of ribonucleotides to desoxyribonucleotides. This enzyme possesses a network of hydrogen-bonded amino-acids through which a hydrogen-atom is transferred to the radical and the active site.[109] This example shows, that hydrogen-bonded phenoxyl-radicals do not have to appear solitary, but can also be part of larger networks. H-bonding of polyradical-polymers can also be used to form well-ordered crystals with bulk magnetic ordering. The manipulation of hydrogen-bonds in these molecules can allow to adjust the magnetic properties of the materials.[110] Another study revealed a direct correlation between the



Scheme 8 Schematic representation of one proposed mechanism for the formation of tyrosyl-radicals.

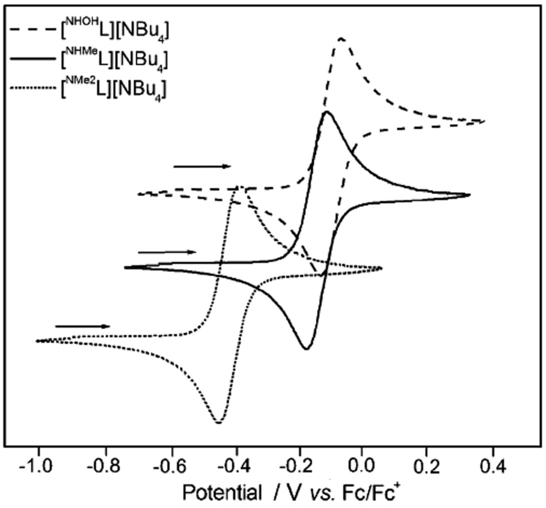


Fig. 4 Cyclic voltammograms of amide–*o*-substituted phenoxyl radical with different substituents (*ca.* 1 mM) in CH_3CN containing 0.2 M $[NBu_4][BF_4]$ at 298 K recorded at a scan rate of 0.1 V s^{-1} (reprinted with permission from ref. 104).

g-value of the radical and the presence of hydrogen-bonding. This easy way to determine the existence of hydrogen-bonding is in particular important, because the H-bonding of a tyrosyl-radical can play an important role for its redox-behavior in biological systems.[30]

Magnetic properties of phenoxy radicals

The characteristics of organic radicals have been studied in-depth for applications using their magnetic properties. These magnetic properties, in the solid state, are determined by intermolecular and intramolecular interactions that depend on the structure of the molecular crystal.[29] Tuning the crystallographic packing represents an effective way to control its magnetic exchange interactions.[111] In some short range-assembled crystals, directed through hydrogen-bonds, crystal geometries can be predictable.[110,111] General predictions of magnetic properties based only on the molecular structure are not possible. Even small changes affect the crystal-packing, which can have major changes of the magnetic behavior.[111] Diradicals possess even more peculiar magnetic properties. The interaction between the unpaired electrons, connected through aromatic moieties, can be tuned to switch between ferromagnetic and antiferromagnetic behavior. Polyradical systems of such compounds were investigated as organic-based memories.[28] Lanthanide-metal ion complexes with radical bridging-substituents have been examined for the use as single-molecule magnets. It has been discovered that already small systems like dimers experience this behavior.[112] Polyradicals of thiophene with phenoxyl-radical moieties possess a rigid conjugation and planar conformation and are a prominent candidate for a high-spin electrically conductive polyradical.[25] Conjugated aryleneethynylene polymers with galvinoxyl-groups as side-chains are also part of this interesting class of conjugated polyradicals (Fig. 5), which possess through space intrachain magnetic interactions.[15]

Galvinoxyl can also be used as polarization agent in the dissolution dynamic nuclear polarization method, which can increase the sensitivity of NMR-measurements several-thousand-fold.[113] As monolayers deposited on gold(111) galvinoxyl-radicals remain stable and appear to be ferromagnetic. In this state the galvinoxyl-radical can still be reversible reduced and oxidized.[114]

Phenoxyl-radicals possess one fatal flaw: they can dimerize or decompose in the solid state. To circumvent this problem molecules with conjugated heterocycles in 4-position have been synthesized. In these compounds the spin-density is even more delocalized, preventing decomposition or dimerization of the radicals.[24] The bulk magnetism of polyradicals does not depend on the spatial arrangement of the molecules, but upon the ability to realize the magnetic interaction of many radical groups through space or covalent bonds. Through these interactions it is also possible to obtain polyradicals that can form a molecule-based magnet without complete conjugation of the polymer. The prime example for this is poly(vinylphenyl(galvinoxyl)).[35] ESR-spectra of this polymers are shown in Fig. 6.

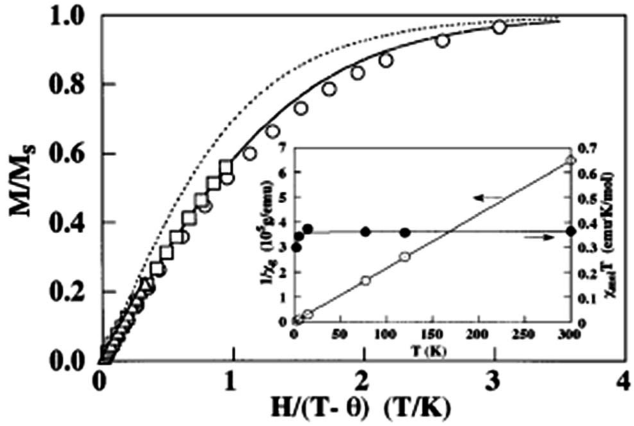


Fig. 5 Normalized plots of magnetization (M/Ms) *vs.* the ratio of magnetic field to effective temperature [$H/(T - \theta)$] for the powder sample of poly(vinylphenyl)galvinoxyl with 65 mol% spin concentration at $T = 2$ (circle), 5 (square), 15 (triangle) K and the theoretical curves corresponding to the $S = 1/2$ (solid line) and 1 (dashed line) Brillouin functions, where θ is a weak antiferromagnetic term and was determined to be −0.3 K from the $1/\chi_g$ *vs.* T plots. Inserted figure: $1/\chi_g$ *vs.* T plots (circle) and $\chi_{mol}T$ *vs.* T plots (filled circle) with the Curie–Weiss fitting (solid lines). (Reprinted with permission from ref. 35.)

Redox-activity and organic radical battery (ORB)

Ever since the first publication by Nakahara *et al.* in 2002 the topic of organic radical batteries has been given a vast amount of attention.[115] ORBs store energy like any other secondary battery by oxidizing the cathode material and reducing the anode-material. The most important difference to commercial batteries are the used electrode-materials, which consist of electroactive polymers that can be reversibly reduced or oxidized hundreds of times and even in a matter of seconds.[14,45] Many publications on this topic deal with cathode-active materials, mostly based on nitroxide-radicals.[14,45,115] The first anodic materials were metals, preferably zinc[116] or lithium.[117] As one of the first non-metallic compounds used as anode material poly(vinylphenyl(galvinoxyl)) was chosen.[31,35,45] Compared to most other phenolic radicals it can store less charge per mass, with a capacity of only 51 mA h g^{-1}, but takes on a special role because of its stability. Unlike other phenoxyl-radicals it does not dimerize nor decompose in solution or in solid state[24] and is essentially insensitive to oxygen.[26] The galvinoxyl-radical can be reversibly reduced to its anionic form at 0.06 V (*vs.* Ag/AgCl) (Fig. 7).

For this reaction an organic base like tetrabutylammonium hydroxide or an alkali butoxide is added to stabilize the anion.[33] In fully organic radical batteries poly(vinylphenyl(galvinoxyl)) is the most used galvinoxyl-based polymer. One of the first organic batteries with galvinoxyl as anode-material was prepared in combination with poly(2,2,6,6-tetramethylpiperidine-1-oxyl methacrylate) (PTMA). The resulting battery had a potential of around 0.7 V. This was also performed in a dry cell with spin-coated layers of the electrode materials. This cell was primarily used as an organic radical memory device.[31] Poly(vinylphenyl(galvinoxyl)) was used in other experiments with 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO)-containing polymers.

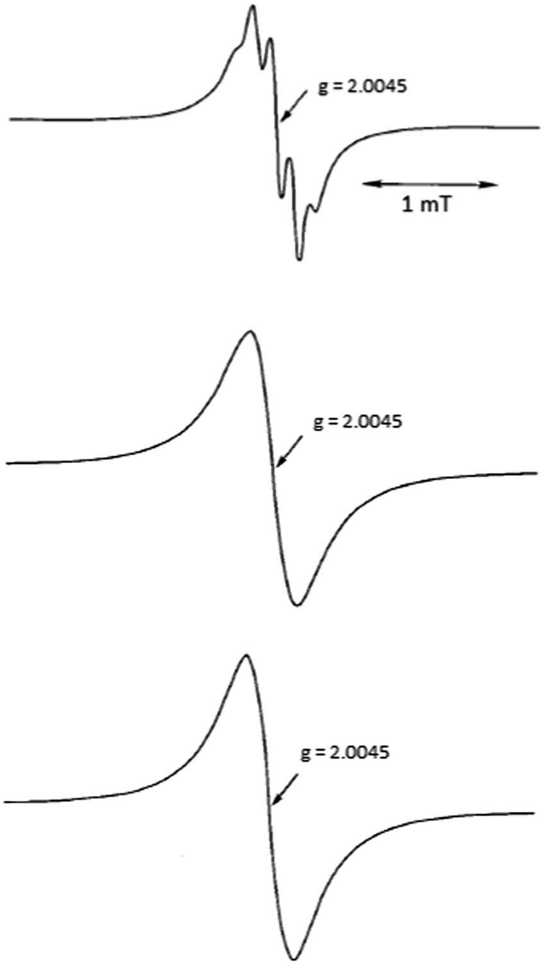


Fig. 6 Solution ESR spectra of poly(vinylphenyl)galvinoxyl in benzene at room temperature with different spin-concentration: (top) 9 mol% (1 monomer unit mmol L^{-1}); (middle) 67 mol% (0.5 monomer unit mmol L^{-1}) and (bottom) 67 mol% (dilution of (b) 0.0005 monomer unit mmol L^{-1}). (Reprinted with permission from ref. 35.)

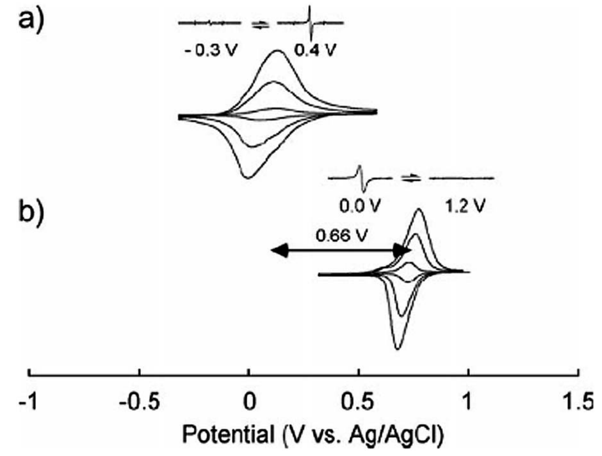


Fig. 7 Cyclic voltammograms of (a) poly(galvinoxylstyrene) and (b) poly(TEMPO-substituted norbornene) films on ITO/glass substrate in 0.2 M $(C_4H_9)_4NClO_4$ acetonitrile solution with 0.01 M tetrabutylammonium hydroxide. Scan rates 1, 5, 10 mV s^{-1} in ascending order (reprinted with permission from ref. 33).

An all-organic battery with a TEMPO-substituted norbornene polymer was prepared. In this battery the capacity dropped slowly from 32 mA h g^{-1} over 250 cycles. A battery with lithium as anode showed even better performance. For 500 cycles a capacity of 42 mA h g^{-1} was held without loss, attributing to the stability of the galvinoxyl-radical.[33] In a battery with poly(nitronylnitroxylstyrene) galvinoxyl displayed once more its special position as extraordinary stable molecule. Even at charging-rates of up to 150 C, which corresponds to a complete charge in 24 seconds, the system only showed a minor drop in capacity (Fig. 8).[44] Galvinoxyl has been incorporated into several polymer-backbones, many of them with conjugated backbones (Scheme 9). Ethynylene-conjugated polymers exist with phenyl bridging-units[68,118,119] or just as poly(phenylene ethynylene).[120] To form chiral structures and to extend the conjugation diethynyl binaphthol has also been incorporated into a polymer, but has not been tested for ORBs.[118,119] Battery-experiments were performed with phenylene ethynylene-polymers with galvinoxyl pendant units. These show the ability of galvinoxyl to perform even in aqueous environments.[120] Several thiophene-based galvinoxyl- as well as phenoxyl-polymers have been synthesized already more than 10 years ago, but were not yet used in ORBs.

These polymers possess good solvent-solubility and processability, because of their 3-substitution on the thiophene. They are prepared by an oxidative polymerization of the thiophene moiety with ferric chloride. Electrochemical measurements of the galvinoxyl-polymer suggested a spin-localization on the galvinoxyl, but not on the polythiophene-backbone.

Further experiments revealed the possibility to create polymers with a localized spin on the galvinoxyl-moiety and a π-delocalizing spin on the thiophenes, forming a bifunctional polyradical with multi-spins and electrical conductivity.[30] Regioregular polythiophenes with pendant phenoxyl-groups

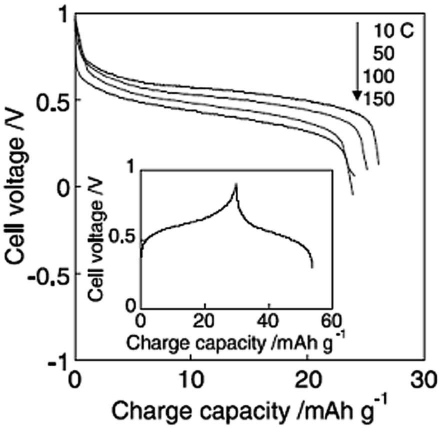
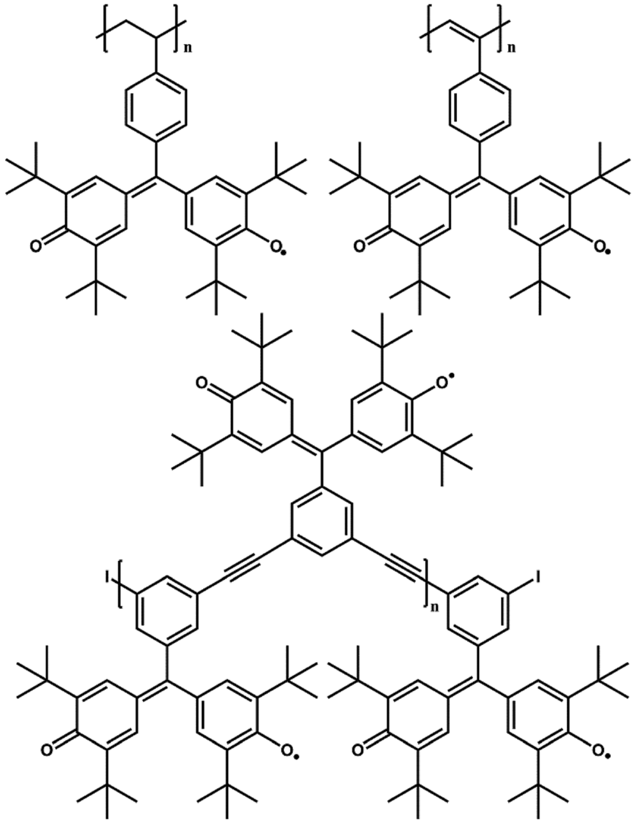
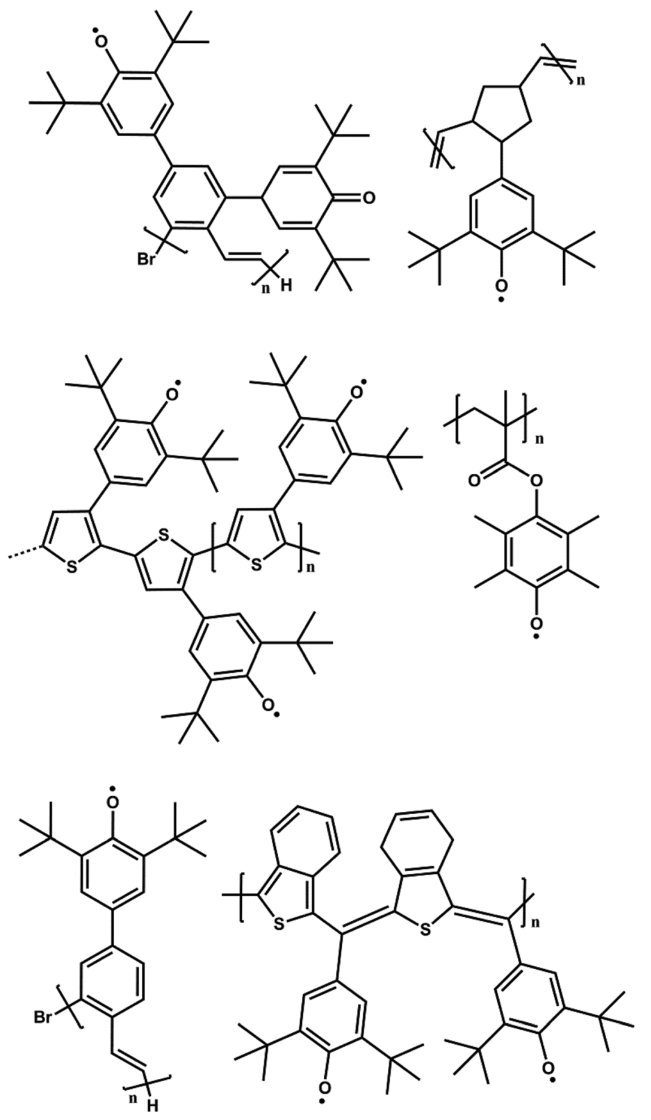


Fig. 8 Charge–discharge curves of a totally organic battery composed of poly(nitronylnitroxylstyrene) and poly(galvinoxylstyrene) in 0.1 M $(C_4H_9)_4NClO_4$ acetonitrile solution with 0.01 M $(C_4H_9)_4NOH$; rate performance of the cell at current densities of 10–150 C rate (reprinted with permission from ref. 44).



Scheme 9 Schematic representation of galvinoxyl-radicals incorporated into different polymer architectures.

exhibit similar properties. The high-spin alignment of these polymers is not sensitive to spin-defect and these π-conjugated radical-bearing polymers are candidates for high-spin, electrically conductive polyradicals.[121] Other high-spin polymers with phenoxyl-groups are mostly conjugated phenylene-vinylene polymers. In these polymers spin-alignment between pendant radicals is not sensitive to spin-defects, which are unavoidable in radical-polymers, because the magnetic interaction is transmitted through the conjugated polymer-backbone.[122,123] The redox-chemistry of all phenoxyl-radicals is similar to that of galvinoxyl. A reversible redox-reaction to the phenolate-anion can be electrochemically induced. This reaction can be observed at around −0.6 V (*vs.* Ag/AgCl). Non-conjugated polymers with methacrylate- or norbornene- backbones have been developed to test this redox-reaction for organic radical batteries (Scheme 10),[124] while conjugated polymers featuring architectures like polythiophene[30,47,50] are mainly studied for their magnetic properties and behavior. Like galvinoxyl the redox-reaction is stabilized by addition of an organic base like tetrabutylammonium hydroxide. These systems give stable charge–discharge behavior up to 100 cycles without much degradation.[124] Substituted nitroxides could also be used as anode-material for ORBs, but are usually more difficult to synthesize.[125] The redox-chemistry of the tocopherol-radical is also strongly dependent on the pH-value and the oxidized species are highly reactive to water.[83] Electrochemical oxidation of α-tocopherol leads to the radical-cation, which dissociates to the radical; the latter one can be further oxidized to the cation. Depending on the applied conditions the redox-potential is either 0.2 V (neutral conditions), 0.5 V (acidic conditions) or −0.8 V (basic conditions; all *vs.* Fc/Fc$^+$).[83] The radical chemistry of tocopherol is characterized by the rate limiting formation of its radical[126] and this primary radical reacts sensitively to subsequent radical species, which changes the EPR-spectrum in a way, that it remains a question if the side chain influences the unpaired electron density.[82] The tyrosyl-radical has not been featured in the research about its redox-activity or for applications in ORBs. Due to the instability of the radical. Two radicals can combine to 3,3′-dityrosine, which is a naturally occurring crosslinked amino-acid.[127,128] Apart from the mentioned the characterization and redox-activity of other phenolic radicals has not been studied in further detail. The development of materials for organic radical batteries based on phenolic radicals is almost exclusively focused on galvinoxyl, with only very



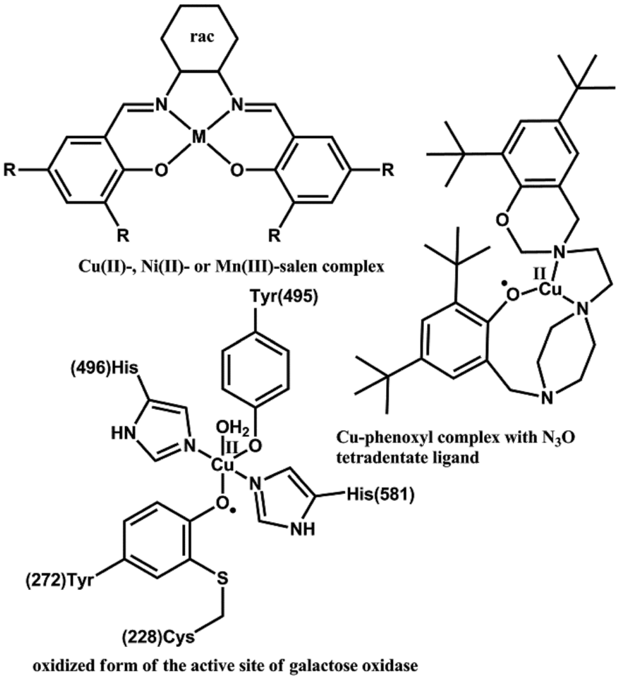
Scheme 10 Schematic representation of phenoxyl-radicals incorporated in a range of polymer architectures.

few examples about other phenolic radicals (*e.g.* phenoxyl-polymers).[124]

Metal complexes containing phenoxyl radicals

Cu-complexes. The book "stable radicals" by Hicks (2010) provided a large recap of metal-coordinated phenoxyl-radicals.[129] Here we extend that collection of phenoxyl-radicals by adding information about recent advances and developments in this field.

Interest in phenoxyl-containing metal-complexes is largely based on the fact that many of these complexes serve as enzyme co-factors for enzymatic reactions in living organisms.[21] The most studied example is the galactose oxidase, which contains one copper ion and conducts the oxidation of a primary alcohol to the aldehyde with oxygen,[23] which is simultaneously reduced to hydrogen peroxide.[16] Other examples of this class of radical enzymes are the glyoxal oxidase or SCO2837p. The connection between all these enzymes is the tyrosyl-radical in the proteins active site.[22] Recreating a whole enzyme to study its function is highly challenging if not impossible. Model complexes mimicking the active center of the enzyme are usually used to emulate the enzyme-activity.[17] The active site of galactose oxidase contains a copper-center with two equatorial histidine ligands, one axial unmodified tyrosine and one equatorial tyrosine, that is cross-linked to an adjacent cysteine residue in an oxidative modification.[18] Several copper-complexes have been synthesized based on this model (Scheme 11), trying to influence the optical and redox properties as well as investigating the effect of the tyrosyl-radical on the enzyme.[16] In a Cu-complex with a tetradentate Schiff-base ligand with a dinaphthylamine backbone superior alcohol-oxidation activity compared to the cyclohexanediamine analogue was reported. The reason for this lays in the increased flexibility of the dinaphthylamine-backbone, which gave access to the Cu(I) oxidation of the catalytic cycle.[130] In the galactose oxidase Cu(II)-salen is a precursor to the persistent phenoxyl-radical. Based upon this several salen phenoxyl complexes were described. Salophen-ligands with a phenylene-diamine spacer are of special interest, because the extended π-system makes the diiminobenzene bridge redox-active and adds a putative oxidation site to the complex.[131]



Scheme 11 Schematic representation of Cu-complexes featuring phenoxyl-radicals.

The incorporation of multiple redox-centers in one molecule can lead to the formation of a metal-ligand radical or a high-valent metal complex on oxidation. In case of most Cu(II)-complexes oxidation leads to a Cu(II)–phenoxyl radical valence tautomer.[132] Another attempt to model the active center was performed using a Cu(II)-complex with N_3O-type-ligands, in which only one phenoxyl-radical is coordinated to the Cu-center. This can undergo a concomitant oxidation of the ligand in the presence of acetonitrile or pyridine. This process occurs through the formation of a Cu(II)–phenoxyl intermediate complex and shows the involvement of the exergonic N-donor ligand to the formation of the phenoxyl-complex.[133] The interest in the mixed-valent state of the oxidized galactose oxidase and the asymmetry of the phenolate-coordination, coupled to the axial/equatorial copper coordination, is very high, because it affects the electronic structure of the tyrosyl radical species. Because of this salen–metal complexes have gotten particular attention, due to being a mixed-valent species resembling the galactose oxidase.[134] This is one of the reasons these complexes are still highly regarded even more than 80 years after their first discovery.[131]

Nitrogen-containing ligands represent popular tools for the generation of phenoxyl–Cu-complexes. Triazole-complexes have shown to stabilize the Cu(I)-form of the complex leading to a diamagnetic ground-state.[135] Pyrazol-containing complexes are also able to stabilize the Cu(I)-form by distorting the coordination around the Cu(II)-ion,[136] as well as, in another

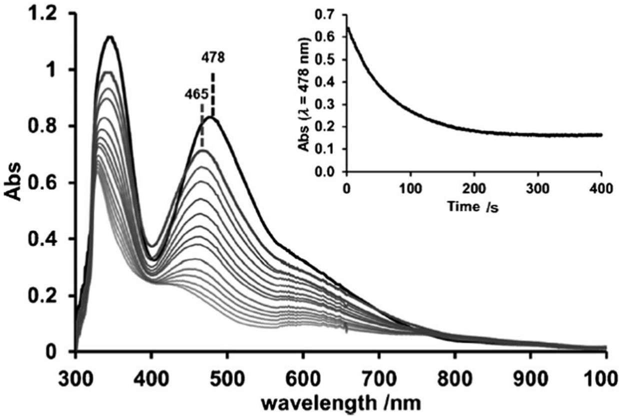


Fig. 9 Reaction between unsymmetric dicopper(II) peroxide complex (0.1 mM) and 4-MePhOH (100 mM) at 183 K. Inset: decay of the UV/Vis band (l = 478 nm) over time, after 4-Me-PhOH addition (reprinted with permission from ref. 138).

configuration, to stabilize by hydrogen-bonding with phenolates.[137] Dimeric copper-complexes with phenoxyl-substituents have also been investigated. The copper-ions in these complexes can be linked by peroxo-groups[138] or chlorides[139] and were all tested in regard to their oxidative activity to achieve the same efficiency as galactose oxidase (Fig. 9). An additional application for these complexes has also been found as potential chemotherapeutic agents. The studied complexes exhibit superoxide dismutase- as well as nuclease-activity.[140]

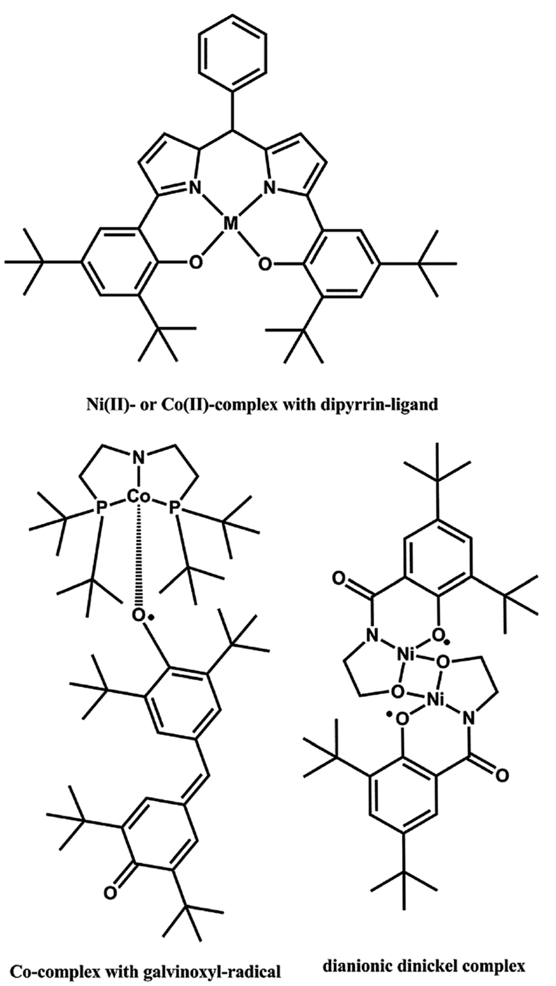
Co- and Ni-complexes. Nickel as well as cobalt can be found in metal–phenoxyl complexes in their +2 or +3 form. Complexes with these metals have been investigated in their one-electron oxidized form (radical) and their two-electron oxidized form. With half-porphyrin ligands the metal center resides in a square-planar geometry, which rules out a formal +3 oxidation of the metal ion.[141] Similar complexes of Ni(II) with trianionic tridentate bridging ligands show that the two oxidations are both ligand-based, leading to the phenoxyl- and diphenoxyl-radicals.[142] In DFT-calculations it has been predicted that the closed-shell possibility of the two-electron oxidized complex lies energetically lower than the triplet state.[141]

Salen-complexes with Ni-ions are also known. In these complexes the salen ligand modulates the electron transfer from the phenolate to the phenoxyl radical using the Ni(II) ion as mediator (Fig. 10).[143] Ni–phenolate complexes have been synthesized as a model compound for the Ni-containing oxidase enzyme acireductone dioxygenase. Unfortunately these complexes are not stable under air or water, but yield several interesting organic products and metal-complexes after decomposition. In this process the organic products originate from the generation of phenoxyl-radicals.[144] While most reported Ni–phenolate complexes are four- or six-coordinated, five-coordinated complexes have been sparsely investigated. Those complexes possess an unsaturated coordination sphere and can offer promise toward the development of novel catalytic systems.[132]

Cobalt(II)-complexes have widespread importance in catalysis, *e.g.*, for ring opening-reactions of epoxides or the oxidation of alcohols. The catalytic ring-opening process of epoxides has been found to be a bimetallic mechanism utilizing a square pyramidal Co(III)-complex and an octahedral Co(III)-complex.[145] Co-complexes with pyrazol-ligands were also investigated in model complexes for galactose oxidase.[136] The range of cobalt-complexes goes from these simple compounds to elaborate 2,6-di-*tert*-butylphenol functionalized clathrochelates and their phenylsulfide-analogues. Those complexes are advertised as fine-tuned and metal-directed antioxidants.[146] Most ligands in Co-complexes of these kind are phenolates and salen-analogues, often described as electron reservoirs, because of their ligand-based redox-cycles.[147] The use of galvinoxyl-radical instead of phenoxyl as radical-ligand in metal complexes is a rarity, but the addition of the galvinoxyl free radical to Co(II)-complexes yields stable compounds.[148]

Fe-, Mn- and other 3d-complexes. Apart from the aforementioned metals, phenoxyl-complexes with the other 3d-metals are much less prominent in literature.

Iron-complexes are present in prostaglandin-*H*-synthases, which catalyze the addition of two equivalents of dioxygen to arachidonic acid during the formation of prostaglandin. As intermediate a tyrosyl-radical is generated, which then transfers an electron to the porphyrin.[149]



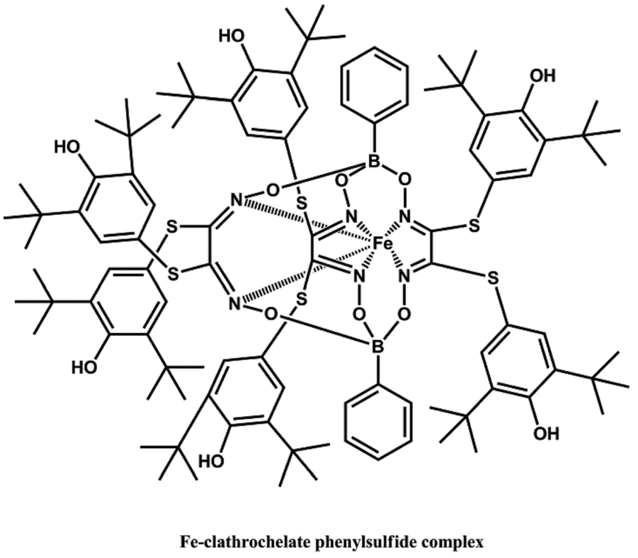
Ni(II)- or Co(II)-complex with dipyrrin-ligand

Co-complex with galvinoxyl-radical

dianionic dinickel complex

Fig. 10 Schematic representations of phenoxyl-bearing complexes with Ni- or Co-center.

Models of Fe–tyrosyl-complexes have been investigated for this enzyme as well as the R2 protein of ribonucleotide reductase. The model for the ribonucleotide reductase contains two iron-ions, a dinucleating bis(carboxylato)-ligand and phenoxyl-radicals stabilized by *tert*-butyl groups.[150] Further enzymes containing Fe-complexes are dioxygenase enzymes. These enzymes utilize mononuclear non-heme iron-centers to activate oxygen molecules to perform oxygenation. Ligand-centered oxidation of these complexes leads to the oxidation of phenolate to phenoxyl-radicals.[151] Stimulus-triggered molecular switching between the ground states represent an interesting application for phenoxyl–Fe-complexes, as such switching leads to detectable electronic and structural changes. Based on models for enzymes like tyrosine hydroxylase or intradiol dioxygenase phenoxyl-containing Fe-complexes were evaluated. The tested species show reversible redox-behavior for 30 cycles with two redox waves, approximately 2 V apart.[152] Like their Co-counterparts complexes of iron with functionalized clathrochelates



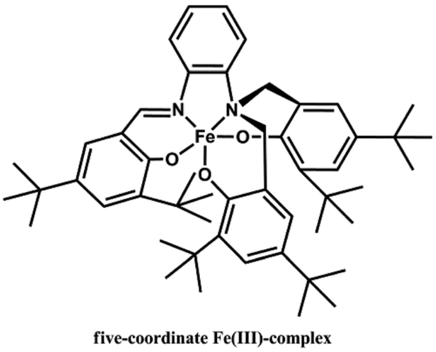


Fig. 11 Schematic representation of Fe-complexes containing phenoxyl-radicals.

were investigated as fine-tuned and metal-directed antioxidants (Fig. 11).[146]

Manganese–salen-complexes were synthesized to investigate the electron-transfer from phenolate to phenoxyl radical in complexes of this kind.[143] Bis–Mn-complexes have been investigated, like their iron-equivalents, in models for a ribonucleotide reductase R2 enzyme[153] and additional Mn–salen and –porphyrin complexes were assessed for their catalytic activity in epoxide ring-opening processes.[154] Cr(III)[155] and Zn(II)[132,156] are rarely used in phenoxyl–metal-complexes, but are nonetheless investigated for their use as catalysts[155] or as model-complexes for enzymes.[132,156]

4d-, 5d- and lanthanide-complexes. Metal complexes with heavy metals are not often utilized with phenoxyl-radical containing substituents. This is caused by the fact that those complexes are usually applied as models for the active center of enzymes; however due the toxicity and size of the heavy metal-ions they are not preferred ingredients for the mentioned applications. Pd–phenoxyl complexes are mainly investigated as catalysts. The effect of electron-withdrawing groups on the catalytic activity of Pd–phenoxyl radicals in the hydrogenation of nitro compounds (Fig. 12)[157] or their use as polymerization-catalysts for vinyl-halides are interesting subjects.[158] In a Ru-complexes phenoxyl-radical is seen as intermediate in a Ru(I)-complex, which reacts rapidly to Ru(II) and phenolate.[159] In a Pt-complex phenoxyl-pyridine is employed to destabilize the metal centered quenching states found in platinum-complexes. The resulting complexes are highly luminescent and emit blue to green light in solution with excellent quantum efficiencies.[160] With dysprosium sandwich-type and triple-decker complexes containing tetrapyrrole- and phenoxyl-ligands have been created for the use as single-molecule magnet application.[161] In other phenoxyl-complexes with either Ln, Sm, Eu, Gd, Tb or Dy as metal-center the luminescent properties of lanthanide nitrate coordination-polymers was assessed.[162]

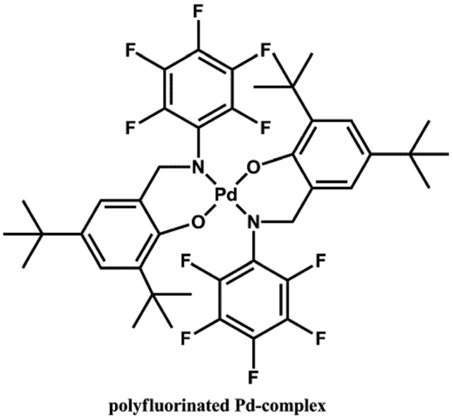


Fig. 12 Schematic representation of a Pd–phenoxyl-complex.

Phenolic radical-compounds in nature (naturally occurring phenols)

Many phenolic compounds are found in plant or animal life. Some of those are oxidized to their phenoxyl-radicals during biological processes or as reaction to some kind of stimulus. This chapter shall provide a small insight about phenolic radicals in flora and fauna.

In many cases phenolic compounds are, like previously described, used as antioxidants or radical scavengers. Resveratrol as antioxidant in grapes[2] or phenolics in apple skin,[97] german chamomile[93] and plums[163] are just a small part of this category. In the seeds of several lupin species,[91] cherimoya peel and pulp[95] or *Helianthemum taxa*,[94] flavonoids are the antioxidative compound. For flavonoids it has been proposed that several structural characteristics are required for antioxidant and radical scavenging activity of flavonoids: An *o*-dihydroxyl-group in the phenyl-ring as well as a conjugated keto-group and a 3-hydroxyl-group in the ring connected to the phenyl-ring.[90] Flavonoids are well-known antioxidants, but can act cytotoxic in larger doses. They can exhibit prooxidant activity in mammalian cells owing to the generation of free radicals and oxidation products.[164] Polyflavonoids are generated by a process catalyzed by oxidases known as laccases. These enzymes can also generate biopolymers for cuticles, lignin or melanin pigments.[165] Gallic acid, cinnamic acid, catechin and quercetin are phenolic antioxidants found in jujube plants. Depending on their species they possess different amounts of these chemicals, but most are known for their medicinal use.[166] Many flavonoids are also found in the human body and are part of mechanisms that prevent inflammatory responses. The reactive oxygen species, generated during these responses, are scavenged by *e.g.* quercetin or catechin and neutralized (Fig. 13).[167]

Phenolic compounds are found in most plants, also those which are not cultivated. The mana-cubiu, native to the Amazonian region, contains at least seventeen carotenoids and three phenolic compounds with radical scavenging capacities.[168] As another class of compounds humic substances effect the fate of organic micropollutants by promoting their phototransformation in aquatic environment.[169] Lignans and related compounds like neolignans can be interesting phenols that possess properties like antiangiogenic, antitumoral and antioxidant activities and are widespread throughout many plants.[170]

A more uncommon phenolic compound is produced when stems of *Vicia faba* are injured. In reaction to this a melanin like compound is generated through the oxidation of 3,4-dihydroxyphenylalanine by phenoxyl radicals of hydroxycinnamic acid esters. Peroxidase enzymes also play part in this reaction, because hydrogen peroxide is also produced.[171] In the phototransformation of phenolic compounds in seawater, phenoxyl-radicals are a common intermediate. They are used in both photonitration and photochlorination processes.[172] An example where phenoxyl-radicals in plants are reduced to their phenolic form is given by a fungus called *Glomerella cingulata*. This fungus causes intense crop losses in mango, papaya, apple and citrus fruits. The plants defenses are neutralized in these cases by an enzyme of the fungus, which reduces generated phenoxyl-radicals and quinones to minimize toxicity.[173] Phenoxyl-radicals, either as stable compound or as intermediate in certain reactions are present in far more plants than the mentioned ones. In most of these cases they are either part of enzymes like galactose oxidase or are used for their radical scavenging and antioxidant capabilities.

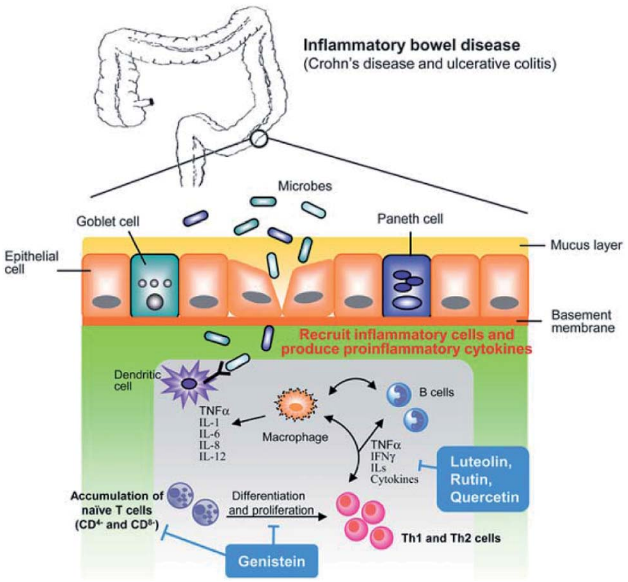


Fig. 13 Underlying mechanisms in inflammatory bowel disease. As bacteria infection or environmental factors that cause colonic endothelium damage result in recruitment of inflammatory and immune cells from bloodstream. Accumulated inflammatory cells produce pro-inflammatory mediators that trigger proliferation and activation of T cells, leading to differentiate to Th1 and Th2 cells that result in amplification of inflammatory cascade and cause tissue injury. Flavonoids act through decreasing inflammatory cytokines production, reducing recruitment of inflammatory cells and modulation of differentiation and proliferation of T cells (reprinted with permission from ref. 167).

Conclusion

Phenoxyl-radicals possess a very broad field of application from radical scavengers and antioxidants to metal-complexes in enzymes, single-molecule magnets and electrode-materials for batteries.

In plants and animals their function as antioxidants has been investigated for many compounds, among those the most prominent are resveratrol, which can be found in grapes, and vitamin E, as well as other tocopherols and tocotrienols. Further examples contain the amino-acid tyrosine, neurotransmitters dopamine and epinephrine or common pain-medications acetylsalicylic acid and paracetamol. The list of examples can be expanded to almost every phenolic compound imaginable. Their primary function is the interception of highly reactive radicals, like hydroxyl-radicals, and the prevention of oxidation in these biological systems.

For investigations of these systems as well as all other applications involving phenoxyl-radicals an extensive knowledge about the structure, stability and reactivity of phenoxyl-radicals has been created. The dependence on bulky substituents on the stability and the influence of hydrogen-bonding on the redox-potential have been investigated in detail as well as bond-dissociation enthalpies and the effects on radical scavenging ability and stability to oxidants.

In metal-centered complexes phenoxyl-radicals, primarily the tyrosyl-radical represents an integral part. Those structures are interesting as models for active centers for enzymes. The most investigated of these enzymes is galactose oxidase. With a central Cu-ion dozens of complexes were synthesized to imitate the enzyme. Several other metal-ions were also investigated in suitable complexes. Phenoxyl-complexes with almost all d-elements exist as models for several enzymes and the number keeps steadily growing.

Another interesting field, which uses phenoxyl-radicals, are organic radical batteries (ORBs). Based on galvinoxyl- or phenoxyl-radicals polymers were synthesized with varyating polymer architectures and evaluated as anode-active battery material. Phenolic radicals can store energy for these batteries by reduction to their anionic form similar to n-type nitroxides.[174] The number of available radicals for this application is limited by the prerequisite of stable radicals, but an increasing range of different compounds has been designed for this field. In the future these polymers may be as important as the

TEMPO-based cathode-materials and an all-organic printed battery can be realized.[175]

Apart from synthetic and industrial applications, phenolic radicals are also very important in many plant species. Here they are mostly used as defensive mechanisms against harmful radiation or radicals, but can also be often intermediates in phototransformation-processes.

The applications for phenolic radicals examined in this contribution correspond to the main uses and sources of phenolic radicals and show an impressive variety in the utilization of phenoxyl-radicals. The topic holds potential for a significant further expansion.

Acknowledgements

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Notes and references

1 K. J. Reszka, D. W. McGraw and B. E. Britigan, *Chem. Res. Toxicol.*, 2009, **22**, 1137–1150.

2 C.-I. Bunea, N. Pop, A. C. Babeş, C. Matea, F. V. Dulf and A. Bunea, *Chem. Cent. J.*, 2012, **6**, 66.

3 A. Bayat and A. Fattahi, *Comput. Theor. Chem.*, 2013, **1018**, 35–44.

4 Y. Y. Thoo, F. Abas, O.-M. Lai, C. W. Ho, J. Yin, R. V. Hedegaard, L. H. Skibsted and C. P. Tan, *Food Chem.*, 2013, **138**, 1215–1219.

5 L.-X. Cheng, X.-L. Jin, Q.-F. Teng, J. Cheng, X.-J. Yao, F. Dai, Y.-P. Qian, J.-J. Tang, X.-Z. Li and B. Zhou, *Org. Biomol. Chem.*, 2010, **8**, 1058–1063.

6 G. Tirzitis and G. Bartosz, *Acta Biochim. Pol.*, 2010, **57**, 139–142.

7 Y. Kadoma and S. Fujisawa, *Molecules*, 2011, **16**, 10457–10470.

8 K. Fukuhara, A. Ohno, I. Nakanishi, K. Imai, A. Nakamura, K. Anzai, N. Miyata and H. Okuda, *Tetrahedron Lett.*, 2009, **50**, 6989–6992.

9 L. Lu, S. Zhu, H. Zhang and S. Zhang, *Comput. Theor. Chem.*, 2013, **1019**, 39–47.

10 K. M. Fabre, K. Saito, W. DeGraff, A. L. Sowers, A. Thetford, J. A. Cook, M. C. Krishna and J. B. Mitchell, *Cancer Biol. Ther.*, 2011, **12**, 915–923.

11 K. Fukuhara, I. Nakanishi, A. Matsuoka, T. Matsumura, S. Honda, M. Hayashi, T. Ozawa, N. Miyata, S. Saito, N. Ikota and H. Okuda, *Chem. Res. Toxicol.*, 2008, **21**, 282–287.

12 A. Tai, T. Sawano, F. Yazama and H. Ito, *Biochim. Biophys. Acta*, 2011, **1810**, 170–177.

13 T. Kawashima, K. Ohkubo and S. Fukuzumi, *J. Phys. Chem. B*, 2010, **114**, 675–680.

14 T. Janoschka, M. D. Hager and U. S. Schubert, *Adv. Mater.*, 2012, **24**, 6397–6409.

15 T. Kaneko, H. Abe, T. Namikoshi, E. Marwanta, M. Teraguchi and T. Aoki, *Synth. Met.*, 2009, **159**, 864–867.

16 Y. Zhang, T. P. Basel, B. R. Gautam, X. Yang, D. J. Mascaro, F. Liu and Z. V. Vardeny, *Nat. Commun.*, 2012, **3**, 1043.

17 P. Verma, R. C. Pratt, T. Storr, E. C. Wasinger and T. D. P. Stack, *Proc. Natl. Acad. Sci.*, 2011, **108**, 18600–18605.

18 K. Ghosh, P. Kumar, N. Tyagi and U. P. Singh, *Inorg. Chem.*, 2010, **49**, 7614–7616.

19 R. P. Pratt, C. T. Lyons, E. T. Wasinger and T. D. P. Stack, *J. Am. Chem. Soc.*, 2012, **134**, 7367–7377.

20 Y. Zhang and J. Stubbe, *Biochemistry*, 2011, **50**, 5615–5623.

21 I. Saberikia, E. Safaei, M. Rafiee, P. Cotic and G. Bruno, *J. Mol. Struct.*, 2012, **1022**, 109–116.

22 F. Thomas, H. Arora, C. Philouze and O. Jarjayes, *Inorg. Chim. Acta*, 2010, **363**, 3122–3130.

23 Y. Shimazaki, T. Yajima, T. Shiraiwa and O. Yamauchi, *Inorg. Chim. Acta*, 2009, **362**, 2467–2472.

24 C. Xie, P. M. Lahti and C. George, *Org. Lett.*, 2000, **2**, 3417–3420.

25 M. Miyasaka, T. Yamazaki, E. Tsuchida and H. Nishide, *Polyhedron*, 2001, **20**, 1157–1162.

26 R. G. Hicks, *Org. Biomol. Chem.*, 2007, **5**, 1321–1338.

27 E. R. Altwickler, *Chem. Rev.*, 1967, **67**, 475–531.

28 V. Barone, C. Boilleau, I. Cacelli, A. Ferretti and G. Prampolini, *J. Chem. Theory Comput.*, 2013, **9**, 1958–1963.

29 K. C. Ko, D. Cho and J. Y. Lee, *J. Phys. Chem. A*, 2012, **116**, 6837–6844.

30 M. Miyasaka, T. Yamazaki and H. Nishide, *Polym. J.*, 2001, **33**, 849–856.

31 Y. Yonekuta, K. Susuki, K. Oyaizu, K. Honda and H. Nishide, *J. Am. Chem. Soc.*, 2007, **129**, 14128–14129.

32 H. Nishide and T. Suga, *J. Electrochem. Soc.*, 2005, **14**, 32–36.

33 T. Suga, H. Oshiro, S. Sugita, K. Oyaizu and H. Nishide, *Adv. Mater.*, 2009, **21**, 1627–1630.

34 X.-J. Qi, L. Liu, Y. Fu and Q.-X. Guo, *Struct. Chem.*, 2005, **16**, 347–353.

35 T. Kaneko, H. Tatsumi, T. Aoki, E. Oikawa, H. Yoshiki, N. Yoshioka, E. Tsuchida and H. Nishide, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 189–198.

36 R. Joshi, S. Kapoo and T. Muhkerjee, *J. Phys. Org. Chem.*, 2007, **20**, 214–220.

37 J. Morales-Roque, M. Carrillo-Cardenas, N. Jayanthi, J. Cruz and T. Pandiyan, *J. Mol. Struct.: THEOCHEM*, 2009, **910**, 74–79.

38 S. N. Mendiara and M. E. J. Coronel, *Appl. Magn. Reson.*, 2008, **33**, 341–349.

39 M. Lucarini, P. Pedrielli and G. F. Pedulli, *J. Org. Chem.*, 1996, **61**, 9259–9263.

40 S. Venu, D. B. Naik, S. K. Sarkar, U. K. Aravind, A. Nijamudheen and C. T. Aravindakumar, *J. Phys. Chem. A*, 2013, **117**, 291–299.

41 C. A. McFerrin, R. W. Hall and B. Dellinger, *J. Mol. Struct.: THEOCHEM*, 2008, **848**, 16–23.

42 S. Barsberg, *Int. J. Quantum Chem.*, 2009, **109**, 1531–1546.

43 C.-W. Cheng, Y.-P. Lee and H. A. Witek, *J. Phys. Chem. A*, 2008, **112**, 2648–2657.
44 T. Suga, S. Sugita, H. Ohshiro, K. Oyaizu and H. Nishide, *Adv. Mater.*, 2011, **23**, 751–754.
45 K. Oyaizu and H. Nishide, *Adv. Mater.*, 2009, **21**, 1–6.
46 D. S. N. Parker, F. Zhang and R. I. Kaiser, *J. Phys. Chem. A*, 2011, **115**, 11515–11518.
47 Y. Innami, R. H. L. Kiebooms, T. Koyano, M. Ichinohe, S. Ohkawa, K. Kawabata, M. Kawamatsu, K. Matsuishi and H. Goto, *J. Mater. Sci.*, 2011, **46**, 6556–6562.
48 H. Nishide, M. Miyasaka and E. Tsuchida, *Angew. Chem., Int. Ed.*, 1998, **37**, 2400–2402.
49 H. Nishide, M. Miyasaka, R. Doi and T. Araki, *Macromolecules*, 2002, **35**, 690–698.
50 M. Miyasaka, T. Yamazaki, E. Tsuchida and H. Nishide, *Macromolecules*, 2000, **33**, 8211–8217.
51 M. Altarawneh, B. Z. Dlugogorski, E. M. Kennedy and J. C. Mackie, *J. Phys. Chem. A*, 2008, **112**, 3680–3692.
52 R. A. Sadykov, G. D. Safina, I. Y. Chukicheva, R. R. Kinzyabulatov and A. V. Kuchin, *Russ. Chem. Bull.*, 2012, **61**, 1667–1668.
53 A. Ueda, S. Nishida, K. Fukui, T. Ise, D. Shiomi, K. Sato, K. Nakasuji and Y. Morita, *Angew. Chem., Int. Ed.*, 2010, **49**, 1678–1682.
54 S. Tero-Kubota, T. Tachikawa, F. Ito, M. Matsui and K. Konishi, *Chem. Phys. Lett.*, 2003, **381**, 340–345.
55 D. R. Albert and H. F. Davis, *J. Phys. Chem. Lett.*, 2010, **1**, 1107–1111.
56 K. A. Freel, M. N. Sullivan, J. Park, M. C. Lin and M. C. Heaven, *J. Phys. Chem. A*, 2013, **117**, 7484–7491.
57 A. T. Maccarone, B. B. Kirk, C. P. Hansen, T. M.Griffiths, S. Olsen, A. J. Trevitt and S. J. Blanksby, *J. Am. Chem. Soc.*, 2013, **135**, 9010–9014.
58 G. I. Khaikin, Z. B. Alfassi and P. Neta, *J. Phys. Chem.*, 1995, **99**, 16722–16726.
59 K. Tanaka, M. Ando, Y. Sakamoto and K. Tonokura, *Int. J. Chem. Kinet.*, 2011, **44**, 41–50.
60 B. B. Kirk, D. G. Harman, H. I. Kenttämaa, A. J. Trevitt and S. J. Blanksby, *Phys. Chem. Chem. Phys.*, 2012, **14**, 16719–16730.
61 M. J. Fadden, C. Barckholtz and C. M. Hadad, *J. Phys. Chem. A*, 2000, **104**, 3004–3011.
62 Z. B. Alfassi, S. Marguet and P. Neta, *J. Phys. Chem.*, 1994, **98**, 8019–8023.
63 C.-W. Zhou, V. V. Kislov and A. M. Mebel, *J. Phys. Chem. A*, 2012, **116**, 1571–1585.
64 R. M. Healy, Y. Chen, I. Kourtchev, M. Kalberer, D. O'Shea and J. C. Wenger, *Environ. Sci. Technol.*, 2012, **46**, 11813–11820.
65 J. F. Orrego, F. Zapata, T. N. Truong and F. Mondragon, *J. Phys. Chem. A*, 2009, **113**, 8415–8420.
66 M. O. Senge, *Z. Naturforsch., A: Phys. Sci.*, 2012, **67b**, 1137–1143.
67 J. Grilj, C. Zonca, L. M. L. Deku and E. Vauthey, *Phys. Chem. Chem. Phys.*, 2012, **14**, 6352–6358.
68 P. Wautelet, P. Turek and J. Le Moigne, *Synthesis*, 2002, **9**, 1286–1292.
69 T. Kaneko, H. Abe, M. Teraguchi and T. Aoki, *Macromolecules*, 2013, **46**, 2583–2589.
70 T. Kaneko, H. Abe, T. Namikoshi, E. Marwanta, M. Teraguchi and T. Aoki, *Synth. Met.*, 2009, **159**, 864–867.
71 H. M. Ali, A. Abo-Shady, H. A. S. Eldeen, H. A. Soror, W. G. Shousha, O. A. Abdel-Barry and A. M. Saleh, *Chem. Cent. J.*, 2013, **7**(53), 1–9.
72 X.-Y. Cao, J. Yang, F. Dai, D.-J. Ding, Y.-F. Kang, F. Wang, X.-Z. Li, G.-Y. Liu, S.-S. Yu, X.-L. Yin and B. Zhou, *Chem.–Eur. J.*, 2012, **18**, 5898–5905.
73 G.-J. Fan, X.-D. Liu, Y.-P. Qjan, Y.-J. Shang, X.-Z. Li, F. Dai and B. Zhou, *Bioorg. Med. Chem.*, 2009, **17**, 2360–2365.
74 Y.-J. Shang, Y.-P. Gjan, X.-D. Liu, F. Dai, X.-L. Shang, W.-Q. Jia, Q. Liu, J.-G. Fang and B. Zhou, *J. Org. Chem.*, 2009, **74**, 5025–5031.
75 L. X. Cheng, J.-J. Tang, H. Luo, X.-L. Jin, F. Dai, J. Yang, Y.-P. Qjan, X.-Z. Li and B. Zhou, *Bioorg. Med. Chem. Lett.*, 2010, **20**, 2417–2420.
76 A. Galano, J. R. Alvarez-Idaboy, M. Francisco-Marquez and M. E. Medina, *Theor. Chem. Acc.*, 2012, **131**(1173), 1–12.
77 R. S. Borges, G. A. N. Pereira, J. K. L. Vale, L. C. S. Franca, M. C. Monteiro, C. N. Alves and A. B. F. da Silva, *Chem. Biol. Drug Des.*, 2013, **81**, 414–419.
78 A. Barzegar and A. A. Moosavi-Movahedi, *PLoS One*, 2011, **6**, e26012.
79 X. Fang, L. Fang, S. Gao and L. Cheng, *Bioorg. Med. Chem. Lett.*, 2013, **23**, 1297–1301.
80 P.-Z. Li and Z.-Q. Liu, *Eur. J. Med. Chem.*, 2011, **46**, 1821–1826.
81 A. Tai, T. Sawano and H. Ito, *Biosci., Biotechnol., Biochem.*, 2012, **76**, 314–318.
82 P. Lehtovuori and H. Joela, *Phys. Chem. Chem. Phys.*, 2002, **4**, 1928–1933.
83 R. D. Webster, *Acc. Chem. Res.*, 2007, **40**, 251–257.
84 G.-X. Li, Z.-Q. Liu and X.-Y. Luo, *Eur. J. Med. Chem.*, 2010, **45**, 1821–1827.
85 I. Nakanishi, K. Fukuhara, T. Shimada, K. Ohkubo, Y. Lizuka, K. Inami, M. Mochizuki, S. Urano, S. Itoh, N. Miyata and S. Fukuzumi, *J. Chem. Soc., Perkin Trans. 2*, 2002, **12**, 1520–1524.
86 A. I. Rey and C. J. Lopez-Bote, *Food Chem.*, 2014, **142**, 342–348.
87 M. Y. Bobrov, A. A. Lizhin, E. L. Andrianova, N. M. Gretskaya, L. E. Frumkina, L. G. Khaspekov and V. V. Bezuglov, *Neurosci. Lett.*, 2008, **431**, 6–11.
88 K. H. S. Farvin and C. Jacobsen, *Food Chem.*, 2013, **138**, 1670–1681.
89 Q. Wang, Y.-P. Qian, F. Dai, D.-L. Lu, W.-J. Yan, Y. Chen and B. Zhou, *Food Chem.*, 2013, **141**, 1259–1266.
90 Y. Rong, Z. Wang, J. Wu and B. Zhou, *Spectrochim. Acta, Part A*, 2012, **93**, 235–239.
91 A. Siger, J. Czubinski, P. Kachlicki, K. Dwiecki and E. Lampart-Szczapa, *J. Food Compos. Anal.*, 2012, **25**, 190–197.
92 X.-Q. Li, J.-B. He, l. Liu and T. Cui, *Electrochim. Acta*, 2013, **96**, 74–81.

93 R. Guimaraes, L. Barros, M. Duenas, R. C. Calhelha, A. M. Carvalho, C. Santos-Buelga, M. J. R. P. Queiroz and I. C. F. R. Ferreira, *Food Chem.*, 2013, **136**, 947–954.

94 A. Rubio-Moraga, J. Argandona, B. Mota, J. Perez, A. Verde, J. Fajardo, J. Gomez-Navarro, R. Castillo-Lopez, O. Ahrazem and L. Gomez-Gomez, *J. Ethnopharmacol.*, 2013, **148**, 287–296.

95 M. R. Loizzo, R. Tundis, M. Bonesi, F. Menichini, V. Mastellone, L. Avallone and F. Menichini, *J. Food Compos. Anal.*, 2012, **25**, 179–184.

96 R. Makino, S. Ohara and K. Hashida, *Holzforschung*, 2011, **65**, 651–657.

97 G. M. Huber and H. P. V. Rupasinghe, *J. Food Sci.*, 2009, **74**, C693–C700.

98 S. P. de Vesser and S. Shaik, *J. Am. Chem. Soc.*, 2003, **125**, 7413–7424.

99 M. J. Zdilla, J. L. Dexheimer and M. M. Abu-Omar, *J. Am. Chem. Soc.*, 2007, **129**, 11505–11511.

100 R. Amorati, S. Menichetti, C. Viglianisi and M. C. Foti, *Chem. Commun.*, 2012, **48**, 11904–11906.

101 M. Orio, O. Jarjayes, B. Baptiste, C. Philouze, C. Duboc, J.-L. Mathias, L. Benisvy and F. Thomas, *Chem.–Eur. J.*, 2012, **18**, 5416–5429.

102 R. Amorti and G. F. Pedulli, *Org. Biomol. Chem.*, 2012, **10**, 814–818.

103 M. C. Foti, R. Amorati, G. F. Pedulli, C. Daquino, D. A. Pratt and K. U. Ingold, *J. Org. Chem.*, 2010, **75**, 4434–4440.

104 R. Wanke, L. Benisvy, M. L. Kuznetsov, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Chem.–Eur. J.*, 2011, **17**, 11882–11892.

105 H. Hernandez-Soto, F. Weinhold and J. S. Francisco, *J. Chem. Phys.*, 2007, **127**, 164102.

106 K. Omura, *J. Org. Chem.*, 2008, **73**, 858–867.

107 M. Bietti and M. Salamone, *Org. Lett.*, 2010, **12**, 3654–3657.

108 S. Itoh, H. Kumei, S. Nagatomo, T. Kitagawa and S. Fukuzumi, *J. Am. Chem. Soc.*, 2001, **123**, 2165–2175.

109 M. Engström, F. Himo, A. Gräslund, B. Minaev, O. Vahtras and H. Agren, *J. Phys. Chem. A*, 2000, **104**, 5149–5153.

110 P. M. Lahti, B. Esat, J. R. Ferrer, Y. Liu, K. A. Marby, C. Xie, C. George, G. Antorrena and F. Palacio, *Mol. Cryst. Liq. Cryst.*, 1999, **334**, 285–294.

111 G. Seber, R. S. Freitas, J. T. Mague, A. Paduan-Filho, X. Gratens, V. Bindilatti, N. Fernandes Olivera Jr, N. Yoshioka and P. M. Lahti, *J. Am. Chem. Soc.*, 2012, **134**, 3825–3833.

112 R. Liu, C. Zhang, L. Li, D. Liao and J.-P. Sutter, *Dalton Trans.*, 2012, **41**, 12139–12144.

113 L. L. Lumata, M. E. Merritt, C. R. Malloy, A. D. Sherry, J. van Tol, L. Song and Z. Kovacs, *J. Magn. Reson.*, 2013, **227**, 14–19.

114 N. Niermann, T. H. Degefa, L. Walder, V. Zielke, H.-J. Steinhoff, J. Onsgaard and S. Speller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **74**, 235424.

115 K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, J. Irijima, M. Suguro and E. Hasegawa, *Chem. Phys. Lett.*, 2002, **359**, 351–354.

116 K. Koshika, N. Sano, K. Oyaizu and H. Nishide, *Chem. Commun.*, 2009, **45**, 836–838.

117 S. Komaba, T. Tanaka, T. Ozeki, T. Taki, H. Watanabe and H. Tachikawa, *J. Power Sources*, 2010, **195**, 6212–6217.

118 T. Kaneko, H. Abe, M. Teraguchi and T. Aoki, *Macromolecules*, 2013, **46**, 2583–2589.

119 T. Kaneko, H. Abe, T. Namikoshi, E. Marwanta, M. Teraguchi and T. Aoki, *Synth. Met.*, 2009, **159**, 864–867.

120 T. Jähnert, B. Häupler, T. Janoschka, M. D. Hager and U. S. Schubert, *Macromol. Chem. Phys.*, 2013, **214**, 2616–2623.

121 M. Miyasaka, T. Yamasaki, E. Tsuchida and H. Nishide, *Macromolecules*, 2000, **33**, 8211–8217.

122 H. Nishide, M. Miyasaka and E. Tsuchida, *Angew. Chem., Int. Ed.*, 1998, **37**, 2400–2402.

123 H. Nishide, M. Miyasaka, R. Doi and T. Araki, *Macromolecules*, 2002, **35**, 690–698.

124 T. Jähnert, B. Häupler, T. Janoschka, M. D. Hager and U. S. Schubert, *Macromol. Rapid Commun.*, 2014, **35**, 882–887.

125 H. Nishide, K. Koshika and K. Oyaizu, *Pure Appl. Chem.*, 2009, **81**, 1961–1970.

126 L. Bamonti, T. Hosoya, K. F. Pirker, S. Böhmdorfer, F. Mazzini, F. Galli, T. Netscher and L. Gille, *Bioorg. Med. Chem.*, 2013, **21**, 5039–5046.

127 L. K. Folkes, M. Trujillo, S. Bartesaghi, R. Radi and P. Wardman, *Arch. Biochem. Biophys.*, 2011, **506**, 242–249.

128 Y. Qin and R. A. Wheeler, *J. Am. Chem. Soc.*, 1995, **117**, 6083–6092.

129 R. G. Hicks, *Stable Radicals, Fundamentals and Applied Aspects of Odd-Electron Compounds*, John & Sons ltd, Chichester, GB 2010.

130 K. Asami, K. Tsukidate, S. Iwatsuki, F. Tani, S. Karasawa, L. Chiang, T. Storr, F. Thomas and Y. Shimazaki, *Inorg. Chem.*, 2012, **51**, 12450–12461.

131 A. Kochem, O. Jarjayes, B. Babtiste, C. Philouze, H. Vezin, K. Tsukidate, F. Tani, M. Orio, Y. Shimazaki and F. Thomas, *Chem.–Eur. J.*, 2012, **18**, 1068–1072.

132 M. Franks, A. Gadzhieva, L. Ghandhi, D. Murrell, A. J. Blake, E. S. Davies, W. Lewis, F. Moro, J. McMaster and M. Schröder, *Inorg. Chem.*, 2013, **52**, 660–670.

133 R. K. Debnath, A. Kalita, P. Kumar, B. Mondal and J. N. Ganguli, *Polyhedron*, 2013, **51**, 222–227.

134 C. T. Lyons and T. D. P Stack, *Coord. Chem. Rev.*, 2013, **257**, 528–540.

135 K. Butsch, A. Klein, S. Nitsche, K. Stirnat, J. R. Hawkett, E. J. L McInnes and M. Bauer, *Dalton Trans.*, 2012, **41**, 11464–11475.

136 G. M. Zats, H. Arora, R. Lavi, D. Yufit and L. Benisvy, *Dalton Trans.*, 2011, **40**, 10889–10896.

137 G. M. Zats, H. Arora, R. Lavi, D. Yufit and L. Benisvy, *Dalton Trans.*, 2012, **41**, 47–49.

138 I. Garcia-Bosch, X. Ribas and M. Costas, *Chem.–Eur. J.*, 2012, **18**, 2113–2122.

139 S. E. Balaghi, E. Safaei, M. Rafiee and M. H. Kowsari, *Polyhedron*, 2012, **47**, 94–103.

140 K. Ghosh, P. Kumar, N. Tyagi, U. P. Singh, V. Aggarwal and M. C. Baratto, *Eur. J. Med. Chem.*, 2010, **45**, 3770–3779.

141 A. Kochem, L. Chiang, B. Baptiste, C. Philouze, N. Leconte, O. Jarkayes, T. Storr and F. Thomas, *Chem.–Eur. J.*, 2012, **18**, 14590–14593.

142 L. Benisvy, R. Wanke, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Eur. J. Inorg. Chem.*, 2011, **18**, 2791–2796.

143 T. Kurahashi and H. Fujii, *J. Am. Chem. Soc.*, 2011, **133**, 8307–8316.

144 T. Deb, G. T. Rohde, V. G. Young Jr and M. P. Jensen, *Inorg. Chem.*, 2012, **51**, 7257–7270.

145 A. Kochem, H. Kanso, B. Baptiste, H. Arora, C. Philouze, O. Jarjayes, H. Vezin, D. Luneau, M. Orio and F. Thomas, *Inorg. Chem.*, 2012, **51**, 10657–10571.

146 A. S. Belov, I. G. Belaya, V. V. Novikov, Z. A. Starikova, E. V. Polshin, A. V. Dolganov and E. G. Lebed, *Inorg. Chim. Acta*, 2013, **394**, 269–281.

147 M. M. Allard, F. R. Xavier, M. J. Heeg, H. B. Schlegel and C. N. Verani, *Eur. J. Inorg. Chem.*, 2012, **29**, 4622–4631.

148 M. J. Ingleson, M. Pink, H. Fan and K. G. Caulton, *J. Am. Chem. Soc.*, 2008, **130**, 4262–4276.

149 E. Matsui, Y. Naruta, F. Tani and Y. Shimazaki, *Angew. Chem., Int. Ed.*, 2003, **42**, 2744–2747.

150 D. P. Goldberg, D. Koulougliotis, G. W. Brudvig and S. J. Lippard, *J. Am. Chem. Soc.*, 1995, **117**, 3134–3144.

151 I. Saberikia, E. Safaei, M. H. Kowsari, Y.-I. Lee, P. Cotic, G. Bruno and H. A. Rudbari, *J. Mol. Struct.*, 2012, **1029**, 60–67.

152 M. M. llard, J. A. Sonk, M. J. Heeg, B. R. McGarvey, H. B. Schlegel and C. N. Verani, *Angew. Chem., Int. Ed.*, 2012, **51**, 3178–3182.

153 A. B. Tomter, G. Zoppellaro, C. B. Bell III, A.-L. Barra, N. H. Andersen, E. I. Solomon and K. K. Andersson, *PLoS One*, 2012, **7**, e33436.

154 T. Kurahashi, A. Kikuchi, T. Tosha, Y. Shiro and H. Fujii, *Inorg. Chem.*, 2008, **47**, 1674–1686.

155 K. Ghosh, P. Kumar and I. Goyal, *Inorg. Chem. Commun.*, 2012, **24**, 81–86.

156 M. Mitra, R. Singh, M. Pyrkosz-Bulska, M. Haukka, E. Gumienna-Kontecka and E. Nordlander, *Z. Anorg. Allg. Chem.*, 2013, **639**, 1534–1542.

157 V. T. Kasumov and E. Sahin, *Spectrochim. Acta, Part A*, 2013, **107**, 31–38.

158 Z. Shen and R. F. Jordan, *Macromolecules*, 2010, **43**, 8706–8708.

159 M. Kuss-Petermann and O. S. Wenger, *J. Phys. Chem. A*, 2013, **117**, 5726–5733.

160 E. Turner, N. Bekken and J. Li, *Inorg. Chem.*, 2013, **52**, 7344–7351.

161 J. Kan, H. Wang, W. Sun, W. Cao, J. Tao and J. Jiang, *Inorg. Chem.*, 2013, **52**, 8505–8510.

162 X.-H. Yan, C.-L. Yi, X.-G. Huang, W.-S. Liu, Y. Tang and M.-Y. Tan, *Inorg. Chem. Commun.*, 2011, **14**, 654–658.

163 N. Miletic, B. Popovic, O. Mitrovic and M. Kandic, *Aust. J. Crop Sci.*, 2012, **6**, 681–687.

164 A. Maroziene, A. Nemeikaite-Ceniene, R. Vidzunaite and N. Cenas, *Acta Biochim. Pol.*, 2012, **59**, 299–305.

165 J.-R. Jeon, P. Baldrian, K. Murugesan and Y.-S. Chang, *Microb. Biotechnol.*, 2012, **5**, 318–332.

166 Q.-H. Gao, C.-S. Wu, J.-G. Yu, M. Wang, Y.-J. Ma and C.-L. Li, *J. Food Sci.*, 2012, **77**, C1218–C1225.

167 M.-H. Pan, C.-S. Lai and C.-T. Ho, *Food Funct.*, 2010, **1**, 15–31.

168 E. Rodrigues, L. R. B. Mariutti and A. Z. Mercadante, *J. Agric. Food Chem.*, 2013, **61**, 3022–3029.

169 S. Kouras-Hadef, A. Amine-Khodja, S. Halladja and C. Richard, *J. Photochem. Photobiol., A*, 2012, **229**, 33–38.

170 V. D. Kancheva, L. Saso, S. E. Angelova, M. C. Foti, A. Slavova-Kasakova, C. Daquino, V. Enchev, O. Firuzi and J. Nechev, *Biochimie*, 2012, **94**, 403–415.

171 U. Takahama and T. Oniki, *J. Plant Res.*, 1998, **111**, 487–494.

172 P. Calza, D. Vione, A. Novell, E. Pelizzetti and C. Minero, *Sci. Total Environ.*, 2012, **439**, 67–75.

173 C. Sygmund, M. Klausberger, A. K. Felice and R. Ludwig, *Microbiology*, 2011, **157**, 3203–3212.

174 T. Jähnert, T. Janoschka, M. D. Hager and U. S. Schubert, *Eur. Polym. J.*, 2014, DOI: 10.1016/j.eurpolymj.2014.06.007.

175 T. Janoschka, A. Teichler, B. Häupler, T. Jähnert, M. D. Hager and U. S. Schubert, *Adv. Energy Mater.*, 2013, **3**, 1025–1028.

Publication P8

P8) "Assorted phenoxyl-radical polymers and their application in lithium-organic batteries"

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Assorted Phenoxyl-Radical Polymers and Their Application in Lithium-Organic Batteries

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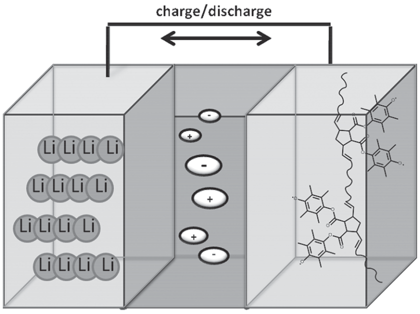
The synthesis and electrochemical characterization of novel polymers bearing phenoxyl-radicals as redox-active side chains is described. The monomers are synthesized from the corresponding phenols and quinones, respectively. These compounds are subsequently polymerized via ring-opening metathesis polymerization. The electrochemical properties of the phenoxyl-radical polymers are characterized using cyclic voltammetry and the most promising polymer is investigated as active material in a lithium coin-cell, creating the first phenoxyl-lithium battery. These phenoxyl-containing polymers represent interesting anode materials for organic radical and lithium batteries due to their suitable redox-potentials and possibility to create batteries with higher potentials as well as straightforward synthesis procedures.



1. Introduction

Phenoxyl-radicals possess a wide field of possible applications, e.g., as antioxidants in plants,[1] integral parts in metal complexes,[2,3] in single-molecule magnetic materials,[4] or as active materials for organic radical batteries (ORBs).[5,6] In plants, phenoxyl-radicals are generated from phenols like resveratrol,[1,7,8] α-tocopherol,[9] or vanillin[10] by oxidation with hydroxyl- and peroxyl-radicals, which are usually generated by ionizing radiation.[11] Most of these radicals are only stable for a very short time and rapidly form dimers;[12] however, there are also some stable radicals (up to several months).[13] Furthermore, phenoxyl-radicals are also often found in metal-complexes as part of enzymes.[14,15] A popular example of this compound is the galactose oxidase.[16–20] Persistent radicals have also been successfully utilized for ORBs. Since the first publication by Nakahara et al. in 2002, many persistent radicals have been synthesized, integrated in polymeric backbones, and tested as electrode-active materials.[21] ORBs started with poly(2,2,6,6-tetramethylpiperidine-*N*-oxyl methacrylate) as cathode-active material and zinc as anode-material.[22,23] Polymeric anode materials are far less common than their cathodic counterparts. The most common anode-active polymer is poly[(*p*-vinylphenyl) galvinoxyl].[6,24] Based on the extremely stable galvinoxyl-radical,[13] several polymeric architectures including polyacetylene,[25] poly(phenyleneethynylene),[26] and polythiophene-based[27] compounds have been synthesized and were tested as active materials for ORBs.[25] These cells usually show good cycling-stability, even in aqueous electrolytes, and are stable in air.[6,25] Other attempts to replace metals in the anode of ORBs and to gain the possibility to achieve higher possible charge- and discharge-rates compared to inorganic materials[28] include the use of poly(viologene)[29,30] and phenoxyl-radicals.[5] These

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polymers possess redox-potentials, which are lower than the potentials of galvinoxyl-containing polymers. The first reported battery using poly(galvinoxylstyrene) as anode-material and TEMPO-functionalized poly(norbornene) as cathode-material exhibited a potential of only 0.6 V,[31] but with the use of poly(viologene) and poly(phenoxyls) potentials of ≈1.3 V can be obtained.[32]

The term phenoxyl-radical is usually not associated with galvinoxyl-radicals, because those radicals inhabit a special category, although they are still technically phenoxyl-radicals.[13] We reported on stable phenoxyl-radical polymers before they were used as electrode-active material in organic batteries. In these cases, the polymer architectures were contributed to the stabilization of the corresponding radical. For this purpose, bulky groups in *para*- and *ortho*-position to the radical were introduced.[13] The utilized substituents in *ortho*-position consisted of *t*-butyl or methyl groups and as polymerizable units in *ortho*-position norbornenes were employed. An advantage of norbornenes is the possibility to introduce them in a variety of ways, e.g., by a Heck-reaction or condensation-reactions,[5] and the simple polymerization conditions. In several test-polymerizations, the polymerization was only hindered by the presence of oxygen and other compounds, e.g., the redox-active moieties seemed to have no or only an insignificant impact. An important goal of this research is to keep the substituents relatively small in order to obtain a high capacity. However, the substituents have to be sufficiently bulky in order to stabilize the phenoxyl-radical and to achieve a reversible redox-reaction.

In this contribution, we use our earlier obtained results with the phenoxyl-bearing polymers as starting point and expand the systems with more functional groups. The employed polymeric architectures of the electroactive polymers are based on poly(norbornene)s. A significant advantage of norbornenes is that they can be polymerized even in the presence of radicals (i.e., as active monomers) and higher molar masses can be obtained.

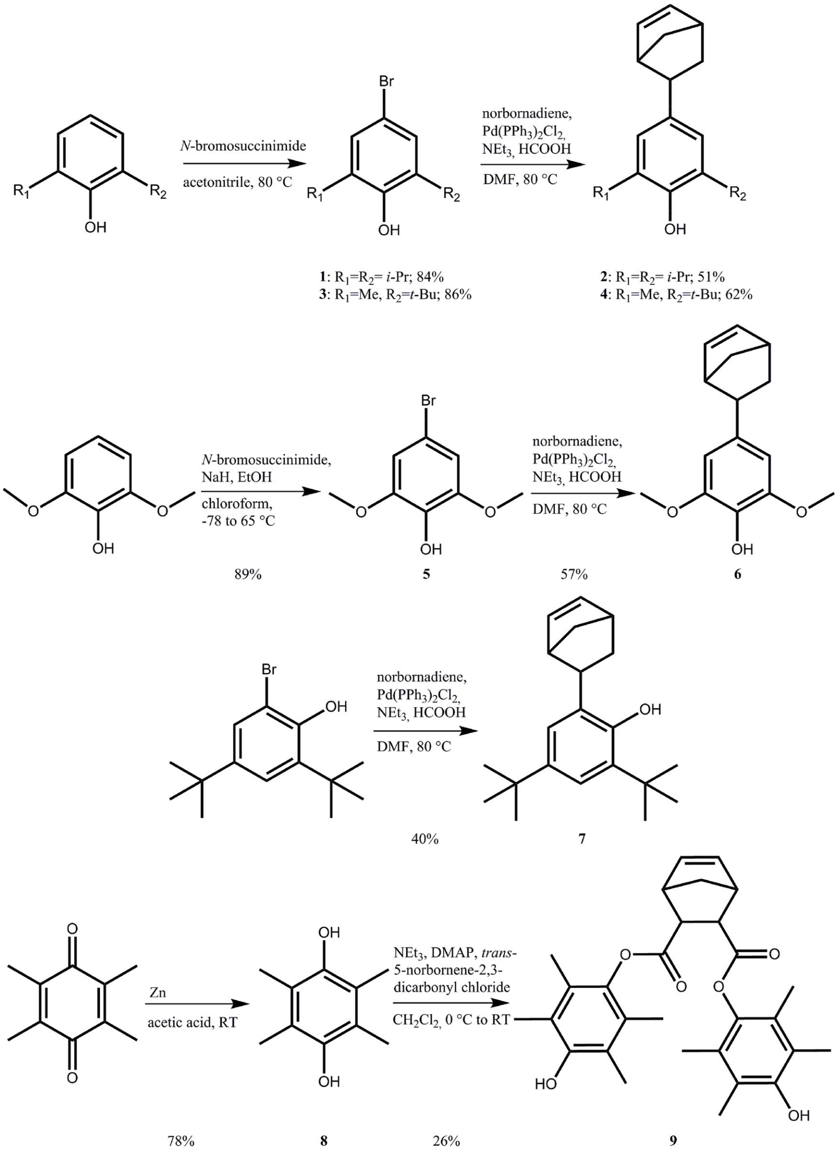
2. Results and Discussion

2.1. Synthesis and Characterization

The examples of phenoxyl-radical bearing polymers in literature are mostly limited to conjugated polymers like poly(thiophene)s[35] or poly(1,2-phenylenevinylene)s.[36] In our approaches, we specifically tried to avoid conjugated systems to keep the redox-reaction localized at the radical-center.[5,32]

The syntheses of the norbornenes **2** and **4** can be performed straightforward in a two-step reaction. The first step is the bromination of propofol and 2-(*tert*-butyl)-6-methylphenol, respectively, with *N*-bromosuccinimide (NBS) to obtain **1** or **3** in very good yields. These *para*-bromo-phenols are subsequently reacted with norbornadiene in a Pd-catalyzed reductive Heck-coupling to obtain the norbornadienes **2** and **4** in yields of 51% and 62%, respectively (Scheme 1). For the synthesis of monomer **6,** a slightly modified approach had to be employed. The bromination of 2,6-dimethoxy phenol was attempted with NBS in acetonitrile as performed for **1** and **3**. However, this reaction only yielded the 3-bromo-substituted phenol and not the desired 4-substituted compound. According to literature, the methoxy-groups have a very strong orienting influence on halogenations, due to being a stronger electron-donator than the phenol-OH, and these halogenations occur usually in meta-position to the phenol and only with an excess of halogenating agent rarely in para-position. It has been determined that with the addition of certain alcohols and sodium hydride the reaction can be pushed toward halogenations in para-position of the phenol.[37] To obtain the desired product the bromination-reaction was performed with NBS, sodium hydride, and ethanol at lower temperatures.[33] This synthesis yielded **5** in 89% yield. The following reductive Heck-reaction was performed similar to the above described procedure and **6** was obtained in 57% (Scheme 1). For the synthesis of **7** no bromination was required because the starting material 2-bromo-4,6-di-*tert*-butylphenol was commercially available and could be immediately converted to its norbornene-equivalent **7** with a yield of 40%. To obtain the *bis*-phenolic monomer **9** different reaction-types were employed. The reduction of duroquinone to the hydroquinone **8** was performed in good yields with zinc/ammonium chloride followed by the esterification of *trans*-5-norbornene-2,3-dicarbonyl chloride with two equivalents of **8** (Scheme 1). To increase the yield of **9** and to prevent mono-substituted compounds 2.1 equivalents of **8** were used.

The ring-opening metathesis polymerization (ROMP) was applied in order to obtain high molar mass polymers. Before the polymerization of the norbornene-monomers **2**, **4**, **6**, **7**, and **9**, all compounds were oxidized with PbO_2 in toluene to receive the corresponding phenoxyl-radicals. Subsequently, the ROMP with the third generation Grubbs-catalyst was performed (Scheme 2). For all polymerizations a monomer to catalyst ratio of 100 to 1 was chosen to obtain polymers with high molar masses. When other catalysts were used, e.g., Grubbs catalyst second generation, insoluble polymers were sometimes obtained due to the relative slow rate of initiation which leads to less polymer-chains of higher molar mass as well as higher possibilities for side-reactions. Also, when higher monomer to catalyst ratios were tested, usually insoluble polymers were obtained due to the resulting higher molar masses.[38] The polymerizations



Scheme 1. Schematic representation of the synthesis of compounds **1** to **9**.

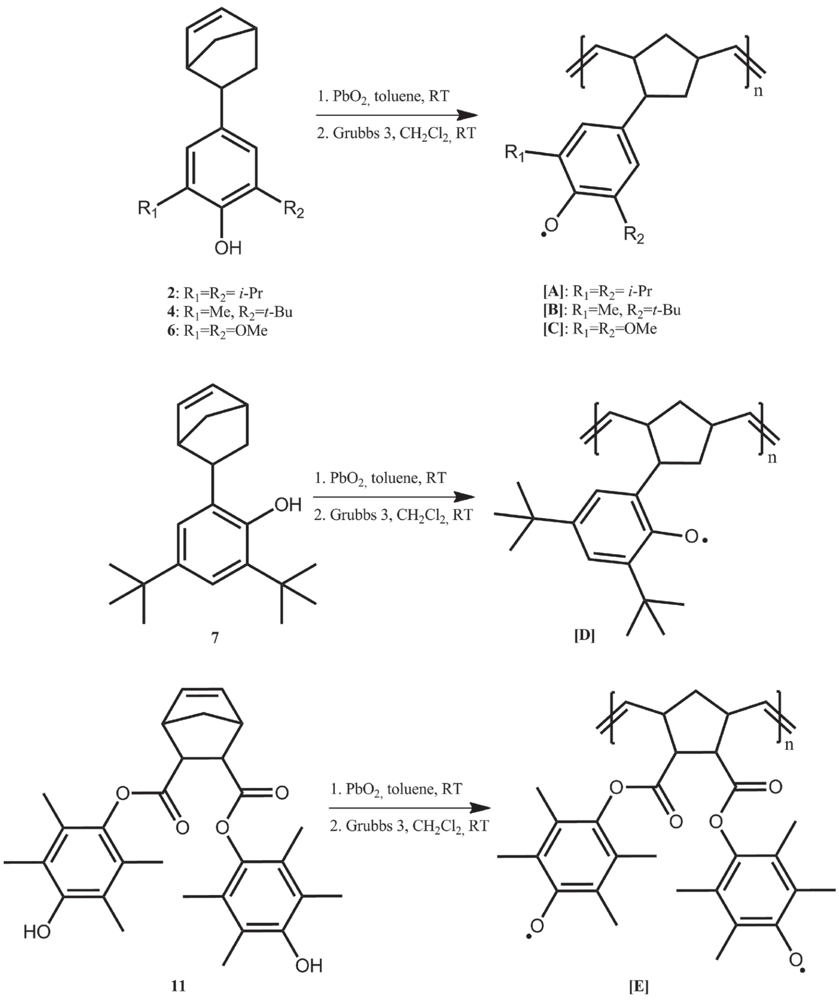
of monomers **2**, **4,** and **6** all yielded polymers with molar masses around 25 000 g mol^{-1} (M_n) and conversions of 90% and above (Table S1, Supporting Information). In all cases, the catalyst was removed by precipitation of the polymers in ethanol. By contrast, the polymerization of monomer **7** was more difficult. In the best case, a yield of 62% for polymer [**D**] was achieved (M_n = 28 400 g mol^{-1}; Đ = 1.12). A reason for this result may be the position of the radical in the ring, which is the major difference to other norbornenes.[34] The small distance of the radical-center to the norbornene ring may cause sterical hindrance with the catalyst and might hinder the polymerization.

The polymerization of monomer **9** was also performed with the oxidized structure. Polymer [**F**] could be obtained with 82% yield (M_n = 22 100 g mol^{-1}; Đ = 1.07) (Table S1, Supporting Information).

2.2. Electrochemistry

The electrochemical properties of all soluble and radical bearing monomers and polymers were investigated by cyclic voltammetry. The redox-active monomers and polymers showed stable CV-signals between –0.55 and –0.67 V (vs Ag/AgCl), depending on their substitution-pattern. All compounds were exposed to up to 30 reduction/oxidation cycles and different scan-speeds without any degradation of the CV-signal (Figure S1, Supporting Information). The alkyl-substituted polymers [**A**] and [**B**] show redox-signals at –0.55 V (vs Ag/AgCl) (Figure 1). This is in accordance with the phenoxyl-polymers reported previously.[5] Polymer [**C**] shows a reversible redox-reaction at –0.64 V (vs Ag/AgCl) (Figure 1). The reasons for this lower potential are the electron-donating methoxy-substituents, which have been introduced instead of the alkyl-substituents. In case of polymer [**D**], the redox-reaction proceeds at –0.60 V (vs Ag/AgCl) (Figure 1). This polymer is similar to our previously reported poly(4-norbornene-2,6-di-*tert*-butylphenoxyl);[5] however, the position of the radical-center is now located between the norbornene- and a *tert*-butyl group and not, as previously situated, between two *tert*-butyl substituents. Polymer [**E**] possesses a redox-potential slightly lower than most of the other polymers at –0.67 V (vs Ag/AgCl). Although the eight methyl-groups in polymer [**E**] act as electron-donating groups the redox-potential is only slightly lower than that of polymer [**A**]. The reasons for this behavior can be related to the carboxyl-units, which act as electron-withdrawing groups and increase the potential.[39] The differences between the two peak-potentials of the polymers are 99 mV for [**A**], 109 mV for [**B**], 87 mV for [**C**], 79 mV for [**D**], and 76 mV for [**E**]. This lets us confirm the reversibility for polymers [**C**] through [**E**] and shows that isopropyl and methyl groups are not enough to stabilize a phenoxyl-radical.

Polymer [**E**] was used to construct a lithium-organic coin-cell battery. This battery was charged and discharged repeatedly at a constant rate. The electrode-reactions are described in Scheme S1 (Supporting Information). The measurements were performed at a rate of 1 C in



Scheme 2. Schematic representation of the polymerization-reactions of phenoxyl radical-monomers.

an argon-atmosphere. A 1 M solution of LiPF$_6$ in propylene carbonate was used as electrolyte. The rate of n C corresponds to a full charge/discharge in 1/n h. ESR-measurements performed beforehand revealed a radical content for the norbornene-polymers of ≈80% (Table S1, Supporting Information), which is in accordance with the reported values.[5,6,40] Further purification attempts to achieve a higher radical-concentration were unsuccessful. Longer reaction times for the oxidation did not yield higher radical concentrations.

The cell shows a stable behavior for charging and discharging at 1 C for 100 cycles. A capacity of 67.1 mAh g^{-1} can be achieved for the first charging and 64.9 mAh g^{-1} for the first discharging cycle. With a theoretical capacity of 112.6 mAh g^{-1}, these results correspond to 60% and 58% of the theoretical values. This slight discrepancy can be attributed to the not fully optimized cell structure, but it is also small enough to show the potential this type of battery holds. In comparison to the radical concentration (Table S1, Supporting Information) about 75% of the radicals are actively used for energy storage. A main focus on improving this value lies in the optimization of the electrode-materials morphology, which plays a large role in giving access to the active material. Another possibility for optimization is the electrolyte, the used salt, and its concentration. The charging-capacity decreases slowly over time, but during the first three cycles the discharge-capacity rises slightly to a maximum of 69.0 mAh g^{-1} and decreases afterward slowly (Figure 2). This might be due to the required equilibration of the cell. After 100 cycles the charge-capacity has decreased to 57.4 mAh g^{-1} and the discharge-capacity to 54.0 mAh g^{-1}. The coulomb efficiency has slightly fallen during this time from 97% during the first cycle to 94% in the 100th cycle. When charging at a rate of 2 C the cell shows a maximum charge-capacity of 67.1 mAh g^{-1} during the second cycle and decreases then more rapidly to 45.6 mAh g^{-1} in the 94th cycle. The discharge-capacity shows similar results with a capacity of 61.9 mAh g^{-1} in the second cycle and a capacity of 42.7 mAh g^{-1} during the 94th cycle (Figure S2, Supporting Information). The degradation of the capacity over the charge and discharge-cycles is not completely described yet, but is most likely a combination of side-reactions of the radical-compound with the electrolyte or its polymer-backbone, slow dissolution of the polymer into the electrolyte or simply ageing.

3. Conclusion

Phenoxyl-radicals have been used scarcely for organic radical batteries. The larger and more stable galvinoxyl-radicals are still the radical of choice for anode-materials. Here, we show the merit of phenoxyl-radicals as electrode-materials for ORBs. Five different polymers based on phenoxyl-radicals have been synthesized and characterized. These polymers were prepared starting from the respective phenols or quinones, using norbornene as polymer-backbone and possessing the stable phenoxyl radical. Reversible redox-reactions at relatively low potentials of −0.6 to −0.8 V (vs Ag/AgCl) could be observed. The stability of the phenoxyl-radicals was shown for a variety of

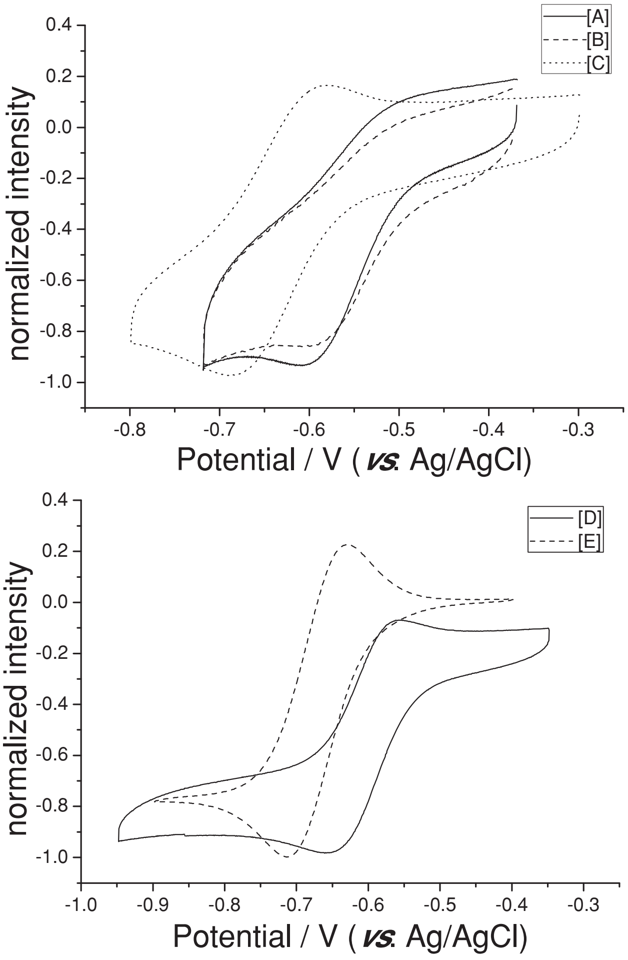


Figure 1. Cyclic voltammogramm of the polymers [**A**] to [**E**] (0.1 V s^{-1}; 0.1 M *n*-Bu$_4$NPF$_6$ in DMF).

different substitution patterns. A representative polymer was chosen and charge-discharge experiments were performed in a lithium-organic battery. The tested phenoxyl-radical polymer showed promising results during these tests, but the results are still subject to improvement by adjusting the electrode-composition and electrode-morphology as well as the electrolyte-composition. Since phenoxyl-radicals possess high capacities at low redox-potentials, they prove to be a valuable class of anode materials for organic radical batteries.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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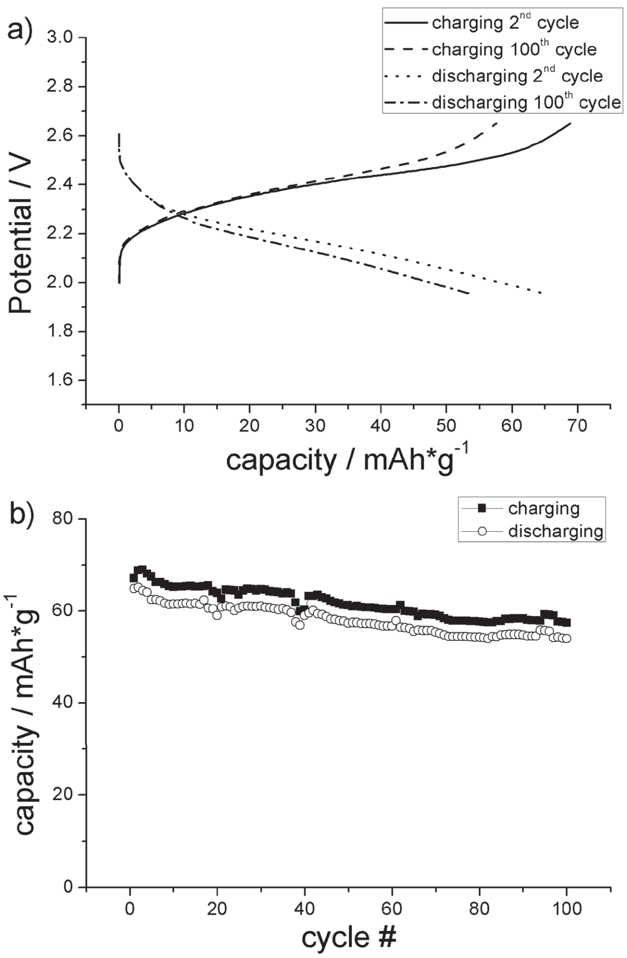

Figure 2. Charge–discharge cycles of polymer [**E**] at 1 C in a lithium-organic coin-cell displayed as a) single cycles and b) as capacities for measured cycles.

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[1] M. Mas-Torrent, N. Crivillers, C. Rovira, J. Veciana, *Chem. Rev.* **2012**, *112*, 2506.
[2] P. Verma, R. C. Pratt, T. Storr, E. C. Wasinger, T. D. P. Stack, *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 18600.
[3] K. Ghosh, P. Kumar, N. Tyagi, U. P. Singh, *Inorg. Chem.* **2010**, *49*, 7614.
[4] R. Liu, C. Zhang, L. Li, D. Liao, J.-P. Sutter, *Dalton Trans.* **2012**, *41*, 12139.
[5] T. Jähnert, B. Häupler, T. Janoschka, M. D. Hager, U. S. Schubert, *Macromol. Rapid Commun.* **2014**, *35*, 882.

[6] T. Suga, S. Sugita, H. Ohshiro, K. Oyaizu, H. Nishide, *Adv. Mater.* **2011**, *23*, 751.
[7] L. Lu, S. Zhu, H. Zhang, S. Zhang, *Comput. Theor. Chem.* **2013**, *1019*, 39.
[8] K. Fukuhara, I. Nakanishi, A. Matsuoka, T. Matsuhara, S. Honda, M. Hayashi, T. Ozawa, N. Miyata, S. Saito, N. Ikota, H. Okuda, *Chem. Res. Toxicol.* **2008**, *21*, 282.
[9] Y. Y. Thoo, F. Abas, O.-M. Lai, C. W. Ho, J. Yin, R. V. Hedegaard, L. H. Skibsted, C. P. Tan, *Food Chem.* **2013**, *138*, 1215.
[10] A. Tai, T. Sawano, H. Ito, *Biosci. Biotechnol. Biochem.* **2012**, *76*, 314.
[11] S. Venu, D. B. Naik, S. K. Sarkar, U. K. Aravind, A. Nijamudheen, C. T. Aravindakumar, *J. Phys. Chem. A* **2013**, *117*, 291.
[12] C. Xie, P. M. Lahti, C. George, *Org. Lett.* **2000**, *2*, 3417.
[13] R. G. Hicks, *Org. Biomol. Chem.* **2007**, *5*, 1321.
[14] I. Saberikia, E. Safaei, M. Rafiee, P. Cotic, G. Bruno, *J. Mol. Struct.* **2012**, *1022*, 109.
[15] F. Thomas, H. Arora, C. Philouze, O. Jarjayes, *Inorg. Chim. Acta* **2010**, *363*, 3122.
[16] Y. Shimazaki, T. Yajima, T. Shiraiwa, O. Yamauchi, *Inorg. Chim. Acta* **2009**, *362*, 2467.
[17] R. C. Pratt, C. T. Lyons, E. T. Wasinger, T. D. P. Stack, *J. Am. Chem. Soc.* **2012**, *134*, 7367.
[18] R. K. Debnath, A. Kalita, P. Kumar, B. Mondal, J. N. Ganguli, *Polyhedron* **2013**, *51*, 222.
[19] S. Itoh, H. Kumei, S. Nagatomo, T. Kitagawa, S. Fukuzumi, *J. Am. Chem. Soc.* **2001**, *123*, 2165.
[20] A. Kochem, O. Jarjayes, B. Baptiste, C. Philouze, H. Vezin, K. Tsukidate, F. Tani, M. Orio, Y. Shimazaki, F. Thomas, *Chem. Eur. J.* **2012**, *18*, 1068.
[21] K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, J. Iriyama, M. Suguro, E. Hasegawa, *Chem. Phys. Lett.* **2002**, *359*, 351.
[22] K. Koshika, N. Sano, K. Oyaizu, H. Nishide, *Chem. Commun.* **2009**, *7*, 836.
[23] S. Komaba, T. Tanaka, T. Ozeki, T. Taki, H. Watanabe, H. Tachikawa, *J. Power Sources* **2010**, *195*, 6212.
[24] H. Nishide, K. Koshika, K. Oyaizu, *Pure Appl. Chem.* **2009**, *81*, 1961.
[25] T. Jähnert, B. Häupler, T. Janoschka, M. D. Hager, U. S. Schubert, *Macromol. Chem. Phys.* **2013**, *214*, 2616.
[26] P. Wautelet, P. Turek, J. Le Moigne, *Synthesis* **2002**, *9*, 1286.
[27] M. Miyasaka, T. Yamazaki, H. Nishide, *Polym. J.* **2001**, *33*, 849.
[28] A. Vlad, N. Singh, J. Rolland, S. Melinte, P. M. Ajayan, J.-F. Gohy, *Sci. Rep.* **2014**, *4*, 4315.
[29] L. Cao, S. Sadaf, S. M. Beladi-Mousavi, L. Walder, *Eur. Polym. J.* **2013**, *49*, 1923.
[30] Y. Takahashi, N. Hayashi, K. Oyaizu, K. Honda, H. Nishide, *Polym. J.* **2008**, *40*, 763.
[31] T. Suga, H. Ohshiro, S. Sugita, K. Oyaizu, H. Nishide, *Adv. Mater.* **2009**, *21*, 1627.
[32] T. Janoschka, M. D. Hager, U. S. Schubert, *Adv. Mater.* **2012**, *24*, 6397.
[33] B. R. Bhattarai, S. Shrestha, S. W. Ham, K. R. Kim, H. G. Cheon, K.-H. Lee, H. Cho, *Bioorg. Med. Chem. Lett.* **2007**, *17*, 5357.
[34] T. Janoschka, A. Teichler, A. Krieg, M. D. Hager, U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 1394.
[35] M. Miyasaka, T. Yamazaki, E. Tsuchida, H. Nishide, *Macromolecules* **2000**, *33*, 8211.
[36] H. Nishide, M. Miyasaka, E. Tsuchida, *Angew. Chem. Int. Ed.* **1998**, *37*, 2400.
[37] J. W. Foley, (Polaroid Corporation, Andover, Mass., USA), *US 4182912*, **1980**.
[38] T. Sukegawa, A. Kai, K. Oyaizu, H. Nishide, *Macromolecules* **2013**, *46*, 1361.
[39] A. Rahman, R. Qureshi, M. Kiran, F. L. Ansari, *Turk. J. Chem.* **2007**, *31*, 25.
[40] T. Kaneko, H. Tatsumi, T. Aoki, E. Oikawa, H. Yoshiki, N. Yoshioka, E. Tsuchida, H. Nishide, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 189.