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

CrossMark

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

Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstr.10, 07743 Jena, Germany
Center for Energy and Environmental Chemistry Jena (CEEC Jena), Friedrich Schiller University Jena, Philosophenweg 7a, 07743 Jena, Germany

ARTICLE INFO

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.

© 2014 Elsevier Ltd. All rights reserved.

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

* Corresponding author. Address: Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstr.10, 07743 Jena, Germany. Tel.: +49 3641948200.

E-mail address: ulrich.schubert@uni-jena.de (U.S. Schubert).

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$_3$)$_2$CN, 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$_5$NO: 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$_5$NO, 304.2116; found, 304.2188.