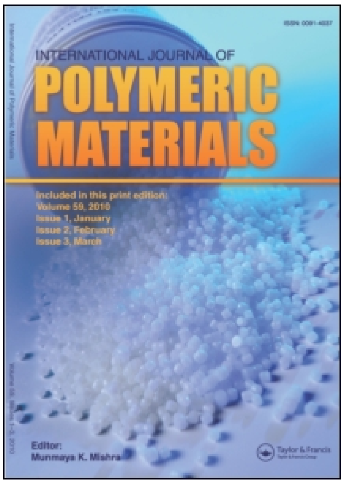

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Preparation, spectroscopic properties and impedance characteristics of a novel ion conducting polymer

Rudolf Pietschnig[a]; Rolf Neuser[a]; Frank Hipler[a]; Tatjana Langkau[b]
[a] Ruhr-Universität Bochum, Bochum, German [b] Institut für Physikalische und Theoretische Chemie, Rheinische Friedrich-Wilhelms Universität Bonn, Bonn, Germany

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PREPARATION, SPECTROSCOPIC PROPERTIES AND IMPEDANCE CHARACTERISTICS OF A NOVEL ION CONDUCTING POLYMER

Rudolf Pietschnig
Rolf Neuser
Frank Hipler
Ruhr-Universität Bochum, Lehrstuhl fü Anorganische Chemie 1,
Bochum, German

Tatjana Langkau
Rheinische Friedrich-Wilhelms Universität Bonn, Institut für
Physikalische und Theoretische Chemie, Bonn, Germany

Preparation and characterization of a novel ion conducting polymeric material (2) is described. The backbone consists of alternating alkenylidene and sulfanylidene units with adjacent hydroxy groups. The material was characterized by elemental analysis, solid state MAS-NMR, IR, UV-VIS and XPS spectroscopy as well as by SEM, dynamic light scattering and complex impedance measurements. Fitting of the experimental data of the impedance measurements in a Bode plot reveals a conductivity of $6.6*10^{-2}$ *S/cm and a capacitance of* $2.2*10^{-5}$ *F at room temperature. The deuterated derivative of 2 shows a significantly lower conductivity, which suggests that the latter can be attributed to proton migration.*

Keywords: ion conductivity, conducting polymer, SEM, impedance

Electrically conducting materials are of considerable interest from scientific and economic points of view [1–4]. Solid electrolytes in particular play an important role in technologically important

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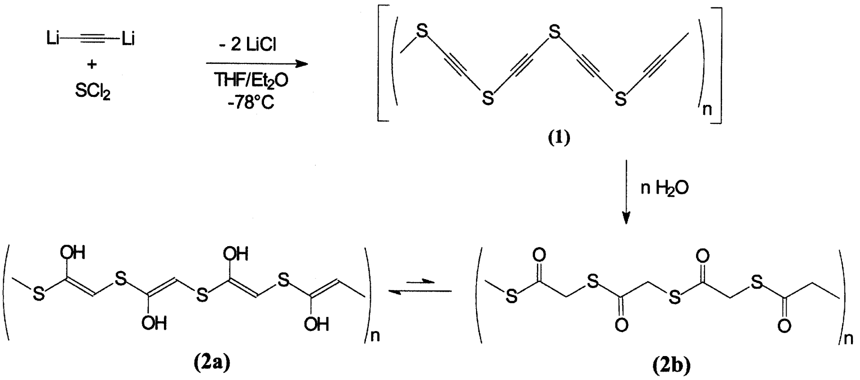
Address correspondence to Rudolf Pietschnig, Ruhr-Universität Bochum, Lehrstuhl für Anorganische Chemie 1, Universitätstraße 150, D-44780 Bochum, Germany. E-mail: rudolf.pietschnig@ruhr-uni-bochum.de

electrochemical systems such as fuel cells or separating media in electrolysis [5]. Despite their importance only a limited variety of basic types of solid polymer electrolytes are known today [6]. These are often expensive and difficult to prepare [7]. Several materials even require elevated temperatures to show significant conductivity [8,9].

In this contribution we would like to present a new, basic type of conducting polymer that is readily synthesized from simple precursors on a laboratory scale. The electrochemical properties of the material obtained in this way are promising for potential application as solid polymer electrolytes at room temperature.

The properties of homoconjugated polymeric materials formed from dimetallated acetylene and dihalosilanes have been investigated intensively regarding their suitability as conducting and preceramic materials [10–12]. In analogy to these results, we investigated the reactivity of dilithio acetylene with sulfur dichloride under similar conditions, which should provide access to a novel conjugated polymer. However, the expected primary condensation product 1 from dilithioacetylene and sulfur dichloride vigorously adds water during the work–up procedure. This results in the formation of polymer 2 in which the bond order between the carbon atoms is reduced compared to 1 and oxy and hydroxy groups are attached to the backbone (Scheme 1). Similar but merely slow addition of water to alkynes, which are activated by the presence of an adjacent thioether group, has been earlier described for related low molecular compounds [13]. Obviously, there should be an equilibrium between two tautomeric forms of each monomeric unit. The spectroscopic data suggest that the enol **(2a)** rather than the keto form **(2b)** is the predominant one.



SCHEME 1 Synthesis of **2**.

Polymer **2** is a powder-like black solid, which is insoluble in all common solvents that we tested. However, it can be readily dispersed in water, ethanol or THF and several other organic solvents. The particle size of a dispersion of **2** in toluene was examined with dynamic light scattering. A wide particle size distribution is observed and the main particle radius varies from 1 μm up to 100 μm. According to X-ray powder diffraction experiments the compound is completely amorphous.

The chemical structure of **2** is consistent with its elemental analysis, XPS, IR and NMR spectra. The absorption of the sulfur atoms (163 eV) in the XPS spectra is indicative for an organo sulfide and also the data for oxygen and carbon corroborate the enol form **2a** [14]. The IR spectra exhibit intense OH vibrational modes (3419 cm^{-1}) and, in contrast, the $>C=O$ modes at 1743 show only weak intensities. Raman spectra could not be obtained, since fluorescence occurs due to strong absorption throughout the whole visible and the near infrared region.

The solid state NMR spectra of **2** also confirm structure **2a.**The ^{13}C CP MAS NMR spectra show even at a spinning rate of 15 kHz a broad unsymmetrical resonance centered at 112 ppm. This shift value fits well in the range for vinylic carbon atoms and would not be consistent with an alkinyl group or the keto isomer. The line width of 3500 Hz is unlikely to be a result of dipolar coupling, since it is independent of the spinning rate. More likely it can be attributed to the wide particle size distribution and a high polydispersity. The proton MAS NMR spectra at a spinning rate of 10 kHz show two major resonances: one relatively sharp signal at 4.8 ppm, consistent with a vinylic proton, and another broad signal centered around 3.0 ppm, which can be assigned to a hydroxy proton. The signal of the CC-H end groups can be detected as well and from the ratio of the vinyl protons and the alkinyl protons M_n can be determined. From the integral of this signal relative to the integral of the vinyl protons, the average chain length was calculated to 3260 repeat units. Due to the insolubility of the material, other methods to determine the molecular weight or the polydispersity of **2** have been unsuccessful so far.

The UV-VIS reflection spectra show two very strong absorption bands at 193 nm and 196 nm. Moreover, continued strong absorption over the UV-VIS range till 700 nm is observed and weaker but still significant absorption until above 1100 nm. This is indicative for extensive conjugation, which would only be possible in isomer **2a**.

Investigation of the dry material with SEM reveals a highly porous structure for **2**, in which globular units with roughly 500 nm to 1 μm diameter form aggregates (Figure 1). These globular units are

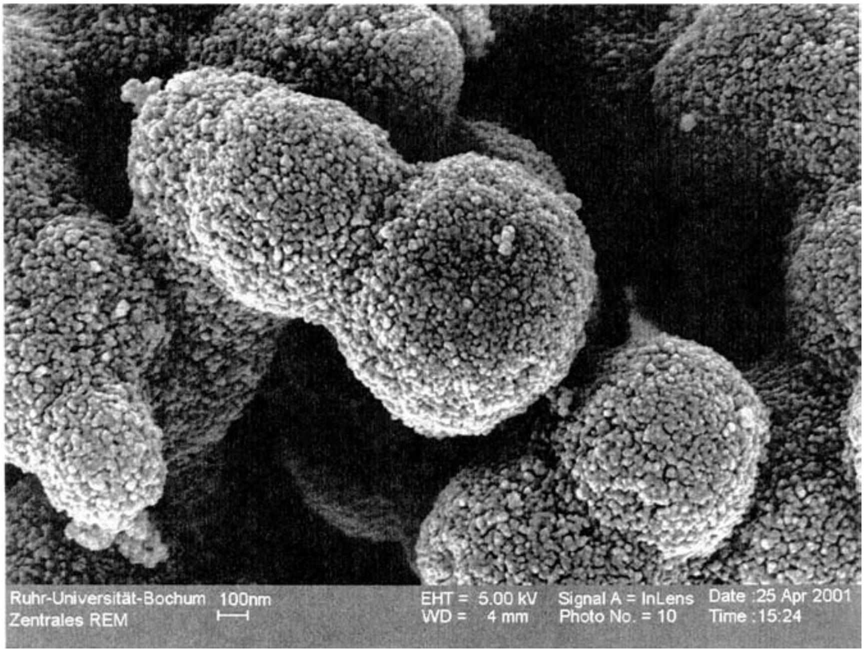


FIGURE 1 Globular units in a scanning electron micrograph of **2**.

themselves constructed from particles of about 10–30 nm in diameter. Findings of broken globular spheres suggest that these units are in fact hollow (Figure 2).

The minimal particle sizes that we found in the dry powder of **2** are smaller than the ones found by dynamic light scattering in toluene suspension. Besides the contribution of solvent molecules to the hydrodynamic radius, this increased particle size in suspension is most likely a consequence of further agglomeration of smaller particles in the presence of solvent.

Complex impedance measurements with the dry powder of **2** were carried out and their results are visualized in a Bode plot (Figure 3). The equivalent circuit that can be fitted to the experimental data consists of an ohmic resist R^1 followed by a constant phase element **Q**, which is parallel to a second ohmic resist R^2 (Scheme 2). From the Bode Plot a conductivity of $6.6*10^{-2}$ S/cm and a capacitance of $2.2*10^{-5}$ F can be calculated.

The indication that proton mobility is the major contribution for the conductivity of **2** can be established experimentally by replacing the H_2O during work–up of the synthesis by D_2O. This material

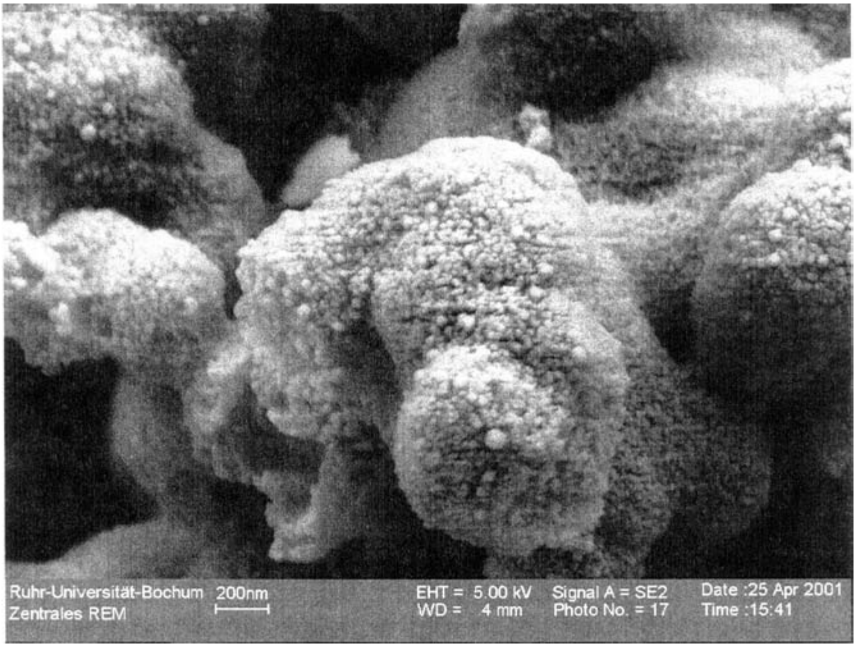


FIGURE 2 Broken hollow spheres in a scanning electron micrograph of **2**.

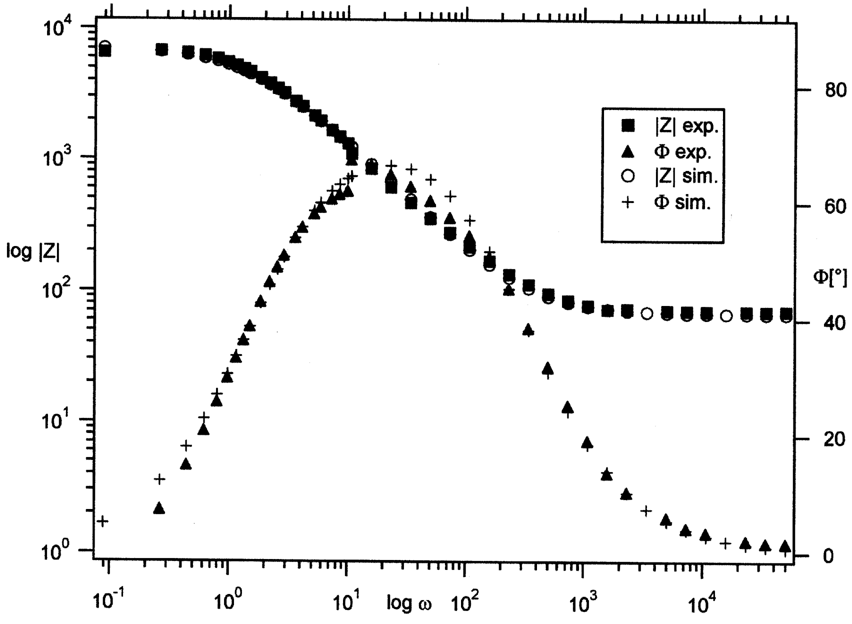
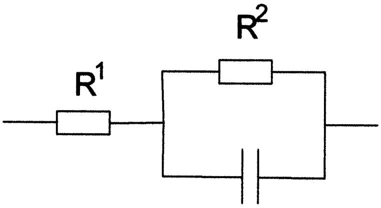


FIGURE 3 Bode plot of fresh **2**; experimental vs. simulated; equivalent circuit (R(RQ)).



SCHEME 2 Equivalent circuit for **2**.

shows a far lower conductivity of only $1.4*10^{-9}$ S/cm. On the other hand, prolonged standing of this low conducting deuterated polymer **3** under ambient atmosphere results in slow D/H exchange and therefore increased conductivity compared to the completely deuterated material.

The low conductivity of the deuterated polymer could be rationalized with an isotopic effect and a higher migration barrier for the heavier D^+ ions versus H^+ ions. Another explanation might be that the keto-enol equilibrium might be different, possibly more in favor of the keto tautomer. Quenching of **1** with a long chain alcohol such as 1-decanol and thereby introducing OR rather then OH groups completely supresses the electric conductivity of the material. Replacing the OH by OR (R = *n*-decyl) groups also leads to soluble polymers, which indicates that the insolubility of **2** does not arise from crosslinking.

We have synthesized a novel electrically conducting material, and characterized the room temperature conductivity with complex impedance measurements. SEM investigations reveal a porous structure consisting of micrometer–sized particles which themselves are built from nanometer–sized units. The solid material behaves from the electrochemical point of view like an electrolyte solution in which proton migration appears to occur easily. The corresponding deuterated material shows a greatly reduced conductivity, which leads to the conclusion that the conductivity can be mainly attributed to proton migration. Investigations of the conduction mechanism and kinetics are currently in progress.

EXPERIMENTAL

The chemical experiments were performed in an argon atmosphere and solvents were freshly distilled prior to use. NMR spectra were recorded on a Bruker DSX 400 and the data were fitted and integrated using the softwere Dmfit98 by Dominique Massiot [15]. IR spectra were obtained using KBr pellets on a Bruker IFS 66. UV/VIS spectra were recorded on a Perkin Elmer Lamda 20 UV/VIS spectrometer in reflective mode using a labsphere RSA-PE-20 detector. SEM data were obtained using a LEO 1530 Gemini. Acquisition details are given at the bottom of each picture. The samples were sputtered with gold before the measurements. XPS data were acquired on a Vacuum Generators UHV system using a CLAM 2 analyzer. Al-K radiation (1486.6 eV) was used for excitation. Impedance spectra were obtained using an impedance system from EG&E (potentiostat 273A, lockin-amplifier 5210). Experimental impedance spectra were fitted using the calculation software “Equivalent circuit” designed by B. A. Boukamp and distributed by EG&E.

Preparation of **2:** A mixture of THF and diethyl ether (1:1) is cooled to $-78°C$ and a solution of n-BuLi in hexanes (60 mmol, 37.5 mL) is added at this temperature while stirring. After 15 minutes, trichloroethene (20 mmol, 2.63 g) is added dropwise. The temperature is maintained for 30 minutes and then the mixture is warmed to room temperature, which leads to precipitation of a white solid (C_2Li_2). Stirring is continued for two hours, after which the mixture is cooled to $-100°C$ and freshly distilled SCl_2 (19 mmol, 2.05 g) in ether (10 mL) is added. The reaction mixture darkens immediately and after seven minutes the cold mixture is poured into distilled water. The dark precipitate is filtered and dried in vacuum. Yield: 4.43 g, 99%.

^{1}H-NMR (400 MHz, 10 kHz rotation): 4.8, 3.0, 1.3 2H; ^{13}C-NMR (100.6 MHz, 15 kHz rotation): 112 ppm. IR(KBr): 3419, OH; 2955, $=CH$;2933, $>CH_2$; 1743, $C=O$. XPS (eV): S: 163; O: 531; C: 284. Analysis for $C_2H_2OS*0.1LiCl$ [%](calcd): $C=32.2$ (32.4); $H=3.1$ (2.9). UV/VIS (nm): continuous absorption 190–1100, maxima at 193, 195, 305 (broad), 400, 500 (very broad).

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