

On the magnetic properties of poly(2-(3,5-diethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-oxide)

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Summary

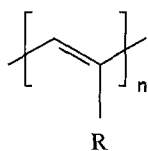
The magnetic properties of poly(2-(3,5-diethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-oxide) (**4**), a polymer with conjugated backbone and stable radicals in side groups, were investigated between 78 and 300 K with magnetic flux densities B between 0.42 and 1.32 Tesla. Samples prepared by evaporation of the solvent from the polymer solution exhibited normal paramagnetism. Samples precipitated by addition of a non-solvent (n-hexane) to a polymer solution showed a dependence of the magnetic mass susceptibility χ_m on B . This behavior is described by superposition of a paramagnetic term and a temperature-independent term depending on B . In addition, an increase of $\chi_m T$ with decreasing temperature T was observed below 150 K.

Introduction

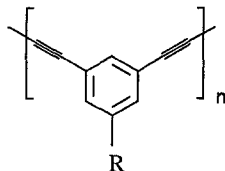
During the past decade the search for organic substances with special magnetic properties has become an interesting field in modern chemistry. Several attempts, based on different theoretical models [1] and computational examinations [2], have been made to prepare purely organic ferromagnetic materials. Until now ferromagnetism has been observed only in rare cases to a low percentage or at very low temperatures. The characterization of the products has often been insufficient. Lack of reproducibility, instability of the products and some theoretical contradictions are main problems discussed in critical papers [3,4]. So a real breakthrough in this industrially interesting field is still to come.

According to the theory of Ovchinnikov [5] and calculations for a "semiempirical AM1 molecular orbital plus configuration interaction model" [2], alternant π -conjugated macromolecules are possible candidates for molecular magnets (cooperative magnetism, high-spin structures etc.) [6,7]. Suitable macromolecules are, for example, poly(acetylenes) (**1**) or poly(diacetylenes) (**2**) with a substituent R having a radical center. Several oligomers and polymers of suitable structure have been synthesized [8-16] but no high-spin structures have been observed.

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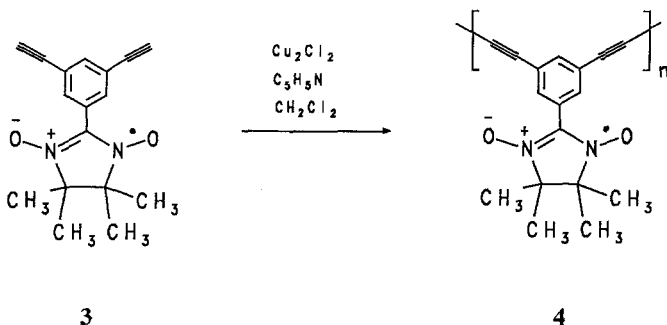


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In a previous paper [17] we described the oxidative coupling of 2-(3,5-diethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-oxide (3) to poly(2-(3,5-diethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-oxide) (4), a polydiacetylene derivative with stable radicals in side groups. Polyradical 4 is a polymer with a conjugated backbone and nitronyl nitroxide side groups. According to the theory of Ovchinnikov [5] the ground-state spin quantum number S of polymer 4 should depend on the polymerization degree n . S should be $1/2$ for $n = 1, 3, 5 \dots$ and 0 for $n = 2, 4, 6 \dots$. But Ovchinnikov's theory is not always successful in the prediction of S , especially in cases comparable to polymer 4 [2]. Thus, polymer 4 is an interesting polyradical from the theoretical point of view.



In the preceding investigation [17], an influence of the workup on the magnetic properties of polymer 4 was found. For samples obtained by addition of a non-solvent (n-hexane) to a polymer solution, the magnetic mass susceptibility χ_m changed when the samples were stored at 78 K for some hours. In contrast to this, samples prepared by evaporation of the solvent exhibited usual paramagnetic properties. This influence of the workup seemed interesting enough to warrant carrying out more detailed investigations. Below we describe further magnetic properties of polymer 4.

Experimental

General and starting materials

The experiments were carried out under dry argon. Pyridine was purified by distillation from potassium hydroxide. CH_2Cl_2 was distilled from P_2O_5 , n-hexane from sodium. Cu_2Cl_2 (p.a.) was from Merck. Monomer **3** was prepared according to Saf et al. [18]. The purification of monomer **3** was accomplished by column chromatography through silica gel (mesh < 230 ASTM) using CH_2Cl_2 as eluent. All substances were stored under dry argon until further reactions or physical measurements were carried out.

Preparation of poly(2-(3,5-diethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-oxide) (**4**)

Monomer **3** (500 mg, 1.80 mmol) was dissolved in dry pyridine (9.0 ml) at 25 °C under argon giving a dark-blue solution. Cu_2Cl_2 (21.0 mg) was added and oxygen was bubbled into the reaction mixture under vigorous stirring. After 4 h the color of the solution was dark-green and a dark greenish-blue solid began to precipitate. CH_2Cl_2 (21.0 ml) was added to dissolve the precipitate. The color changed to dark-blue. Oxygen was bubbled into the solution for an additional 26 h; the solvent mixture evaporated was continuously substituted by addition of CH_2Cl_2 . The copper salts were removed by filtration with a G4 frit. The dark-blue solution of polymer **4** in CH_2Cl_2 /pyridine was divided into two portions of approximately equal volume.

One portion was slowly evaporated under reduced pressure at 20 °C to give sample *A* (205 mg). A dark-green film was obtained. The other portion was slowly poured into n-hexane (250 ml). The precipitated solid was filtered off and dried rapidly in vacuo to give sample *B* (198 mg), a powder with a turquoise-blue color.

Sample *A* (30 mg) was dissolved in dry CH_2Cl_2 (10 ml) at 25 °C under argon. The solution was slowly poured into n-hexane (100 ml). The precipitated solid was filtered off and dried rapidly in vacuo to give sample *C* (28 mg). A powder with a turquoise-blue color was obtained.

Sample *B* (30 mg) was dissolved in dry CH_2Cl_2 (10 ml) at 25 °C under argon. The solution was slowly evaporated under reduced pressure to give sample *D* (30 mg), a dark-green film.

Instrumental equipment

IR, UV and ESR spectroscopy and gel permeation chromatography (GPC) were carried out as described previously [17]. The magnetic susceptibility χ_m was measured under helium atmosphere in the range 78 to 300 K (starting temperature 300 K, average cooling rate 2.2 K/min) at magnetic flux densities of 0.42, 0.71, 1.02 and 1.32 Tesla on a modified Faraday balance SUS 10, Paar AG (Graz, Austria); calibration was carried out with freshly prepared $\text{HgCo}(\text{SCN})_4$. For diamagnetic correction, the precursor substance of monomer **3**, 2-(3,5-diethynylphenyl)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine (**5**), was prepared [18].

The diamagnetic mass susceptibility $\chi_{m, \text{dia}}$ of imidazolidine **5** was determined as $-7.55 \cdot 10^{-9}$ m^3/kg .

Results and discussion

Characterization

For polymer **4**, the maximum of the molecular weight distribution was approximately 6200 g/mol [17]. No significant differences between the IR, UV and ESR spectra of samples A to D and those already published [17] could be detected. A discussion of the ESR spectra of the solid samples A to D will be published elsewhere [19].

Magnetic properties

The magnetic behavior of samples A and D was identical. *Fig. 1* shows a plot for sample A. The product $\chi_m T$ of A and D was a linear function of the temperature T with no significant dependence on the magnetic flux density B. Extrapolation of $1/\chi_m$, as a function of T, to T = 0 K gave no significant deviations from Curie's law. This is the Curie-Weiss law, see Eq. (1), with $\theta = 0$ K. Thus samples A and D exhibited normal paramagnetic properties, no more ordered spin states were observed. On the theory of ideal paramagnetic behavior (the orbital angular momentum being neglected), the paramagnetic mass susceptibility $\chi_{m, p}$ was calculated by Eq. (2).

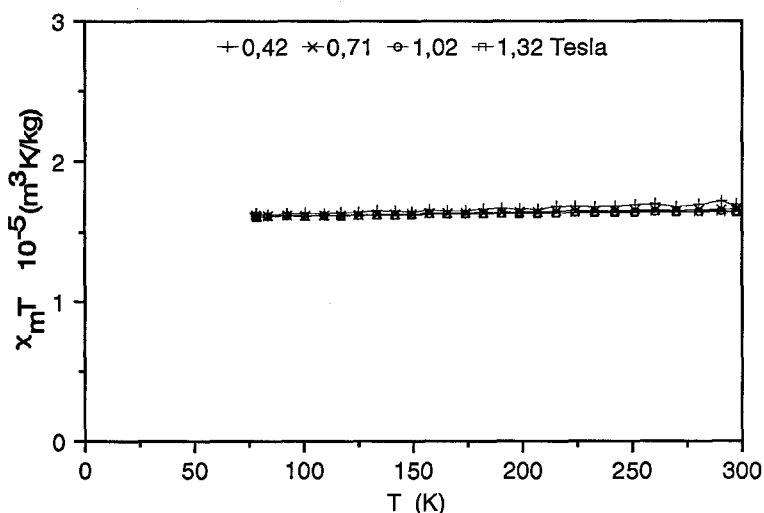


Fig. 1. $\chi_m T$ as function of T for sample A

$$\chi_m = \frac{C}{(T-\theta)} \quad (1)$$

$$\chi_{m,p} = \frac{N_A \rho_o g^2 \mu_o \mu_B^2 S(S+1)}{3MkT} \quad (2)$$

The calculation for sample *A* and *D* was made with $S = 1/2$, $M = 279.32$ g/mol (for the repeating unit of polymer **4**) and $g = 2.00657$, measured in solution, as approximation [17]. The other units have their usual meanings (for example $\mu_B = 9,2741 \cdot 10^{-24}$ J/T). The experimental values of the Curie constant C corresponded, within experimental error, to those calculated. The mean value of the experimental constant was $C_{exp} = 1.63 \cdot 10^{-5}$ m³K/kg, whereas the calculated constant was $C_{calc} = 1.69 \cdot 10^{-5}$ m³K/kg.

Sample *B* exhibited completely different and anomalous magnetic properties, as shown in *Fig. 2*. $\chi_m T$ was not a linear function of T and depended on the magnetic flux density B . Thus the magnetic behavior could not be described by Eq. (1) with a constant value of θ . Sample *C* showed magnetic properties similar to those of sample *B*, see *Fig. 3*. The same trends can be seen.

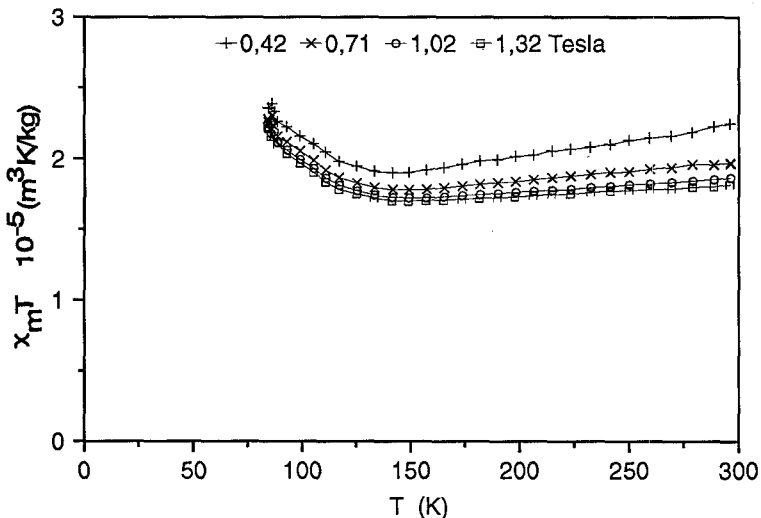


Fig. 2. $\chi_m T$ as function of T for sample *B*

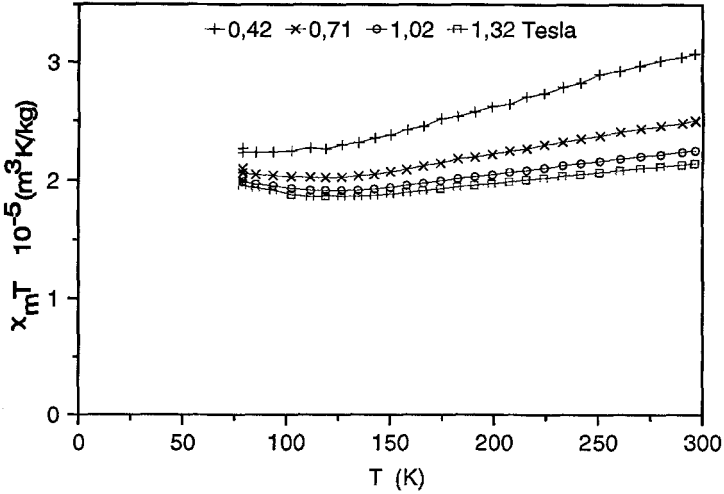


Fig. 3. $\chi_m T$ as function of T for sample C

For both samples $\chi_m T$ depended on B . In the range 150 to 300 K, $\chi_m T$ was a linear function of T and the data in *Fig. 2* and *Fig. 3* were described by Eq. (3); X , Y = constants depending on the sample. χ_m is subdivisible into a term $\chi_{m,p}$ depending on T and a term $\chi_{m,B}$ depending on B , see Eq. (4).

$$\chi_m = \frac{C}{T} + \frac{X}{B} + Y = \chi_{m,p} + \chi_{m,B} \quad (3)$$

$$\chi_{m,B} = \frac{X}{B} + Y \quad (4)$$

The term $\chi_{m,p}$ describes the paramagnetic properties. The term $\chi_{m,B}$ incorporates the magnetism of a more ordered spin-state. As an approximation we used the $\chi_{m,p}$ values obtained for sample A (ideal paramagnetic behavior) in calculating $\chi_{m,B}$ for samples B and C . *Fig. 4* shows $\chi_{m,B}$ as function of T in the range 150 to 300 K for the samples B and C .

The constants X and Y are $8.81 \cdot 10^{-9} \text{ m}^3 \text{ T/kg}$ and $1.25 \cdot 10^{-9} \text{ m}^3/\text{kg}$ for sample B and $2.01 \cdot 10^{-9} \text{ m}^3 \text{ T/kg}$ and $1.25 \cdot 10^{-9} \text{ m}^3/\text{kg}$ for sample C (Eq. (4)). Magnetic behavior similar to Eq. (3) is usually interpreted as the effect of ferromagnetic impurities on the measurement of paramagnetic susceptibilities [20].

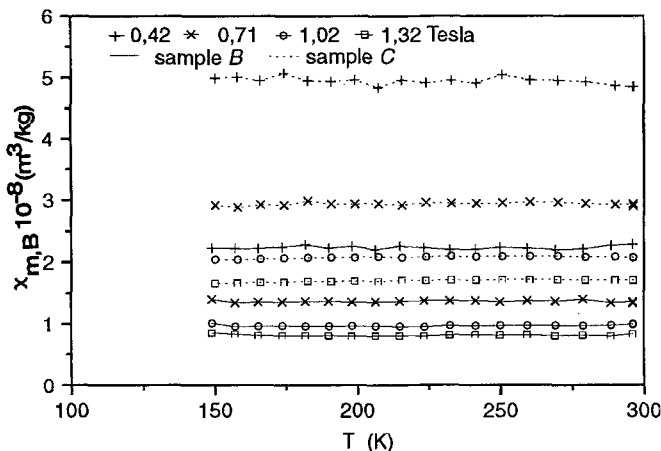


Fig. 4. $\chi_{m,B}$ as function of T for sample B and C

Below 150 K both samples show values of $\chi_m T$ increasing with decreasing T, see Fig. 2 and Fig. 3. The increase is greater for sample B than for sample C. One reason for the differences observed between sample B and C could be that the precipitation conditions were not fully identical as described above.

The constants X and Y and the increase of $\chi_m T$ below 150 K were not very reproducible. Sometimes samples of the type B and C showed only very small constants X and Y and nearly no increase of $\chi_m T$. There were some indications that the spread of the curves in Fig. 2 and Fig. 3 was influenced by the rate of drying of the precipitate. It was also not possible to substitute the n-hexane in the precipitation by certain other non-solvents.

$\chi_{m,B}$ should be zero for ideal paramagnetism and no increase of $\chi_m T$ with decreasing T should be observable. It may thus be concluded that cooperative types of magnetism occur in polyradical **4** depending on the precipitation conditions. Since the samples A to D were prepared from the same batch, magnetic impurities, especially traces of metal ions such as iron, and chemical reactions during the workup can both be excluded as cause of the different magnetic properties.

The main result of the present investigation is that for suitably precipitated samples of the polyradical **4** the magnetic susceptibility depends on the magnetic flux density. To a minor extent, we have also observed this behavior for other conjugated polyradicals [21].

Acknowledgments

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