polymer reports

Influence of the precipitation method on the magnetic properties of a polyradical with conjugation in the backbone and nitronyl nitroxide side groups

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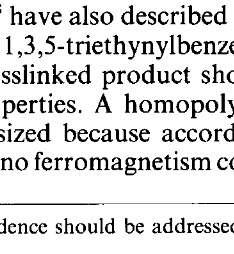
2-(3,5-Diethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-oxide (**1**) was polymerized by oxidative coupling to poly(2-(3,5-diethynylenephenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-oxide) (**2**), which was characterized by gel permeation chromatography, spectroscopic methods (infrared, ultraviolet, electron spin resonance), transmission electron microscopy and magnetic susceptibility measurements. Samples of polymer **2** obtained by evaporation of the solvent showed the usual paramagnetic properties while those obtained by addition of a non-solvent to a solution exhibited an increase of the magnetic mass susceptibility χ_m when the samples were stored at a temperature of 78 K.

(Keywords: conjugated polymer; polyradical; nitroxide; precipitation; magnetic properties)

INTRODUCTION

Nitroxides are possible candidates for organic materials with special magnetic properties[1–8]. Poly(2-(4-ethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-oxide) and poly(4-(4-ethynylbenzylideneamino)-2,2,6,6-tetramethylpiperidine-1-oxyl) were described previously and showed only normal paramagnetic or antiferromagnetic behaviour[6,7].

2-(3,5-Diethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-oxide (**1**), a nitronyl nitroxide, is another interesting monomer for the preparation of paramagnetic or even ferromagnetic materials. Its synthesis was worked out by Miura and Inui[8] but a much higher yield was achieved by our group[9].



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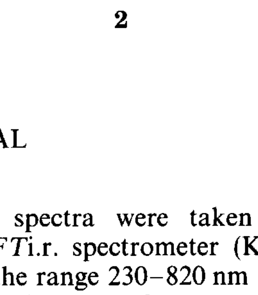
Miuri and Inui[8] have also described the copolymerization of **1** with 1,3,5-triethynylbenzene by oxidative coupling. The crosslinked product showed only normal paramagnetic properties. A homopolymer of monomer **1** was not synthesized because according to the theory of Ovchinnikov[10] no ferromagnetism could be expected.

In the present paper we deal with the preparation and properties of the homopolymer, poly(2-(3,5-diethynylenephenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-oxide) (**2**). The magnetic behaviour, measured with the magnetic mass susceptibility χ_m, depends on the precipitation method.



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EXPERIMENTAL

Instruments

Infrared (i.r.) spectra were taken on a Bomem Michelson 100 *FT*i.r. spectrometer (KBr). Ultraviolet (u.v.) spectra in the range 230–820 nm were taken from solutions in CH_2Cl_2 on an Omega spectrophotometer from Bruins Instruments. χ_m was measured under helium in the thermal range 78–300 K at magnetic flux densities of 0.42, 0.71, 1.02 and 1.32 T on a modified Faraday balance SUS 10, Paar AG (Graz, Austria); calibration was carried out with freshly prepared $HgCo(SCN)_4$. For diamagnetic correction, the precursor substance

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of monomer **1**, 2-(3,5-diethynylphenyl)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine (**3**), was prepared[9]. The diamagnetic mass susceptibility χ_{dia} of **3** was determined as -7.55×10^{-9} m^3 kg^{-1}. A Merck-Hitachi L-6000 pump was used as liquid chromatograph for gel permeation chromatography (g.p.c.) with CH_2Cl_2 as eluent. The absorption was recorded with an Altex model 152 dual wavelength u.v. detector at 254 nm. The columns used (PL gel 10 μ, 10^4 Å; 10 μ, 500 Å) and the polystyrene standards ($M_w = 730$, 11 500, 81 500, 455 000, 1 560 000) were from Polymer Lab. Ltd. Electron spin resonance (e.s.r.) spectra were taken on a Bruker ER 200 D X-Band spectrometer; the g values were determined by using Fremy's salt ($g = 2.005\,50 \pm 0.000\,05$) as reference. Transmission electron microscopic (TEM) images were taken on a Philips 200 kV CM20/STEM.

Materials

Pyridine was purified by distillation from potassium hydroxide. CH_2Cl_2 was distilled from P_2O_5, *n*-heptane from sodium. Cu_2Cl_2 (p.a.) was from Merck. The purification of monomer **1** was accomplished by column chromatography through silica gel (mesh <230 ASTM) using CH_2Cl_2 as eluent. All substances were stored and all reactions were carried out under dry argon.

Preparation of polymer 2

A sample of monomer **1** (172 mg; 0.62 mmol) was dissolved in 3.0 ml of dry pyridine at 25°C under argon giving a dark-blue solution. Cu_2Cl_2 (7.0 mg) was added and oxygen was bubbled into the reaction mixture under vigorous stirring. After 4 h the colour of the solution was dark-green and a dark-green/blue solid started to precipitate. CH_2Cl_2 (7.0 ml) was added to dissolve the precipitate. The colour changed to dark-blue. Oxygen was bubbled into the solution for an additional 26 h. Undissolved copper salts were removed by filtration. The dark-blue solution was divided into two parts of approximately equal volume.

One part was slowly evaporated under reduced pressure at 20°C to give 73 mg of sample A. The other part was slowly poured into 100 ml of *n*-heptane. The precipitated solid was filtered off and dried rapidly *in vacuo* to give 69 mg of sample B.

I.r. spectrum (KBr): 3084, 2980, 2938, 2219 (–C≡C–), 1579, 1453, 1392 ($N\dot{-}O$), 1360 ($C(CH_3)_2$), 1217, 1172 ($N\dot{-}O$), 1134 ($N\dot{-}O$), 890, 860 cm^{-1}.

U.v. spectrum ($\lambda(\varepsilon)$, λ in nm, ε in l mol^{-1} cm^{-1}, calculated on the repeating unit of the polymer): 264 (14 476), 277 (15 117), 297 (16 464), 317 (18 068), 339 (15 438), 373 (4385), 580 (107).

RESULTS AND DISCUSSION

Polymer **2** was prepared by the catalysed oxidative coupling of the terminal ethynyl groups of **1** with Cu_2Cl_2 and O_2, a common reaction for the preparation of polydiacetylenes[11].

G.p.c. was used to examine the progress of the reaction. Calibration with polystyrene standards was carried out for determination of molecular weight. This is an approximation because the structures of the polymers are different. In *Figure 1*, curve a belongs to monomer **1**. Oligomers with increasing molecular weight are present in curves b, c and d. After a reaction time of 30 h (curve e) no residual monomer **1** could be detected. The maximum of the molecular weight distribution in curve e was approximately 6200 g mol^{-1}. This corresponds to a polymerization degree of about 22 monomeric units, indicating successful coupling of monomer **1**. The molecular weight distribution depended greatly on the purity of monomer **1** and on the solvent. The use of a mixture of pyridine and CH_2Cl_2 as solvent for the coupling reaction increased the solubility of polymer **2** and yielded higher molecular weights in comparison to other solvents.

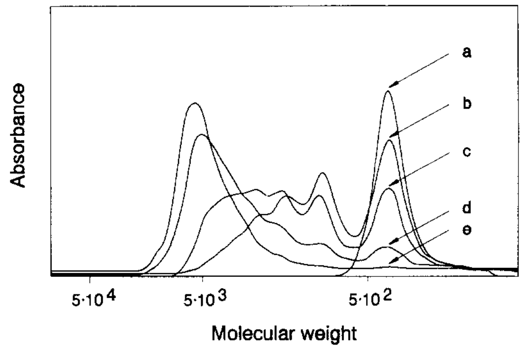

Figure 1 Molecular weight distribution during the reaction of monomer **1** to polymer **2**. Reaction times (h): a, 0; b, 2; c, 6; d, 12; e, 30 h

Figure 2 E.s.r. spectrum of polymer **2** ($c = 2.0 \times 10^{-4}$ mol l^{-1}, calculated on the repeat unit of the polymer) in CH_2Cl_2

The strong i.r. absorptions of monomer **1** at wavelengths of 3302 and 3285 cm^{-1}, typical for terminal ethynyl groups, disappear completely in the spectrum of polymer **2**. The polymer shows an additional weak absorption at 2219 cm^{-1} due to the substituted –C≡C– bond. Polymer **2** still shows the typical absorptions of nitronyl nitroxides at 1392 and 1172 cm^{-1}. Thus no significant side reactions of the nitronyl nitroxide groups occurred during the reaction.

The u.v. spectrum of polymer **2** dissolved in CH_2Cl_2 showed the typical absorption of nitronyl nitroxides near 370 nm.

The e.s.r. spectrum of polymer **2**, measured in CH_2Cl_2, shows a broad absorption with a g-value of 2.006 57, see *Figure 2*.

The dependence of χ_m of monomer **1** on the temperature T shows no deviation from Curie's law:

$$\chi_m = C/(T - \theta) \qquad (1)$$

where $\theta = 0$ K (θ is the paramagnetic Curie temperature).

On the theory of ideal paramagnetic behaviour (the orbital angular momentum being neglected), the theoretical paramagentic mass susceptibility of monomer **1** was calculated by equation (2):

$$\chi_m = N_A \rho_0 g^2 \mu_0 \mu_B^2 S(S+1)/3MkT \qquad (2)$$

where $S=1/2$, $M=281.33$ g mol^{-1} and, as an approximation, $g=2.006\,57$; the other symbols have their usual meanings. The experimental values corresponded to those calculated, within experimental error ($C_{exp}=1.633\times10^{-5}$ m^{3}K kg^{-1}; $C_{theor}=1.679\times10^{-5}$ m^{3}K kg^{-1}).

The main result of the present investigation is that the magnetic properties of polymer **2** depend on the methods for making the solid samples for the measurements. For example, two samples A and B were made.

Sample A. The solvent CH_2Cl_2/pyridine was completely evaporated. A dark-green film was obtained. TEM images showed a diffuse structure.

Sample B. The solution in CH_2Cl_2/pyridine was poured into *n*-heptane. A powder with a turquoise-blue colour was obtained. It consisted of small spnerules, see the TEM image in *Figure 3*.

χ_m of sample A was measured while decreasing T from 300 to 78 K with an average cooling rate of 2.2 K min^{-1}. $\chi_m T$ is a linear function of the temperature T according to *Figure 4a*. Extrapolation of $1/\chi_m$ as a function of T to $T=0$ K gave no significant deviations from Curie's law. The values of χ_m and their temperature dependence are close to theory for ideal paramagnetism calculated according to equation (2). The calculation was made with $S=1/2$, $M=279.32$ g mol^{-1} (repeat unit of polymer **2**) and $g=2.006\,57$ (approximation). The χ_m value of sample A remained constant even after 5 h at 78 K.

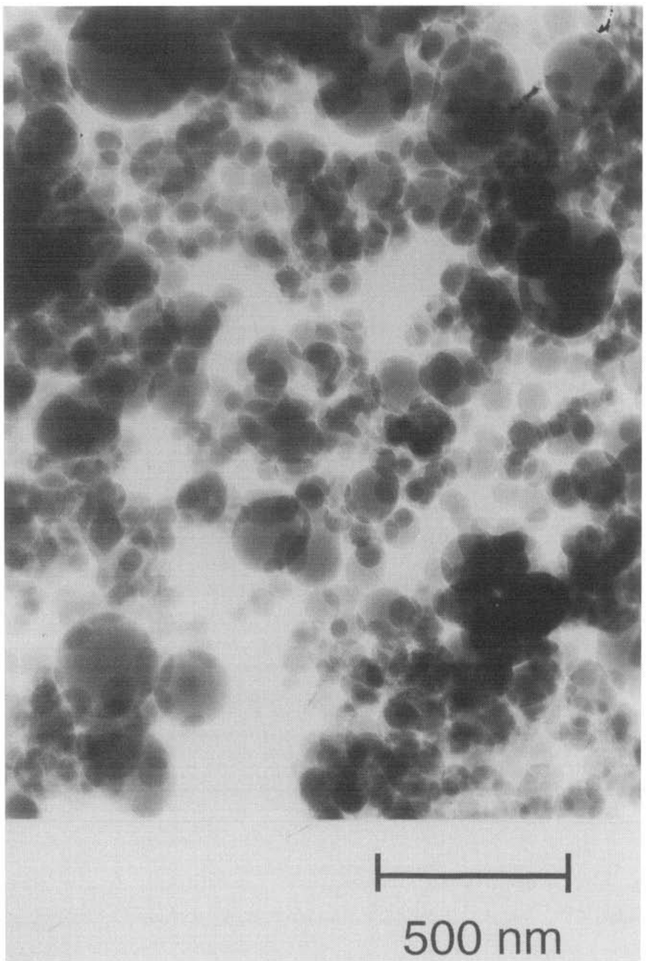

Figure 3 TEM image of polymer **2**, sample B

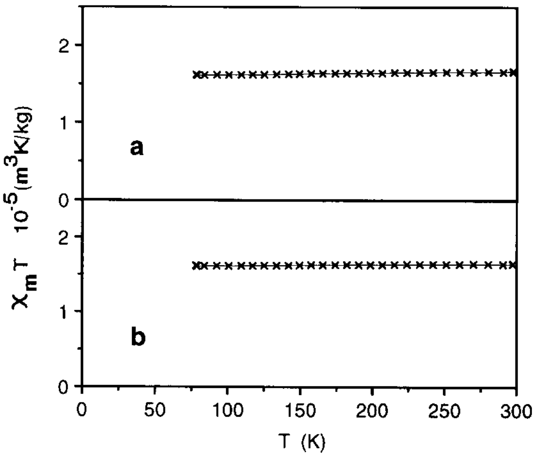

Figure 4 $\chi_m T$ as a function of temperature T for sample A (a) and sample B (b) (starting temperature 300 K, average cooling rate 2.2 K min^{-1})

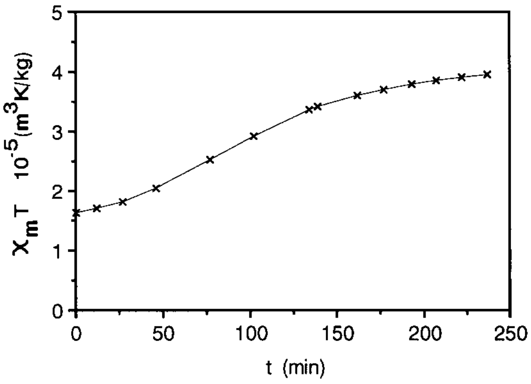

Figure 5 Increase of $\chi_m T$ of sample B as a function of time t ($T=78$ K)

The χ_m value of sample B was determined under the same conditions (300 to 78 K with an average cooling rate of 2.2 K min^{-1}). The results obtained corresponded to those of sample A within experimental error, see *Figure 4b*. At the final temperature, $T=78$ K, χ_m was measured for an additional 240 min. *Figure 5* shows the dependence of $\chi_m T$ on the time t. $\chi_m T$ increased from 1.64×10^{-5} to 3.97×10^{-5} m^{3}K kg^{-1}. This increase was not very reproducible; the values of $\chi_m T$ after 240 min varied between 2.30×10^{-5} and 3.97×10^{-5} m^{3}K kg^{-1}. There were some indications that the differences were influenced by the rate of drying of the precipitate. After 240 min at 78 K, χ_m was measured while T was slowly increased to 300 K (average heating rate in the thermal range 78–160 K, 1 K min^{-1}; 160–220 K, 4 K min^{-1}; 220–300 K, 8 K min^{-1}). *Figure 6* shows that $\chi_m T$ is no longer a linear function of T. For $T>160$ K the experimental values correspond to those shown in *Figure 4b*.

Since samples A and B 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 causes of the different magnetic properties.

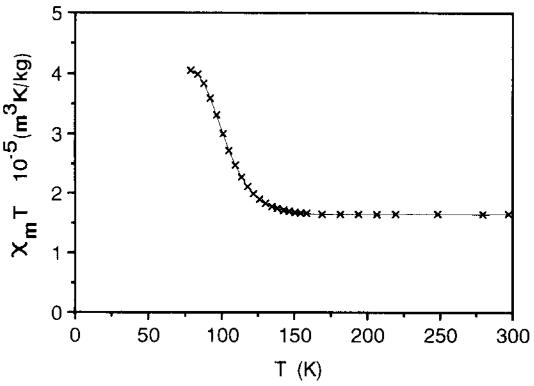

Figure 6 $\chi_m T$ as a function of temperature T for sample B after 240 min at $T = 78$ K (average heating rate in the thermal range 78–160 K, 1 K min^{-1}; 160–220 K, 4 K min^{-1}; 220–300 K, 8 K min^{-1})

It may be concluded that cooperative types of magnetism occur in polyradical **2** at low temperatures depending on the precipitation conditions. Furthermore the investigations demonstrate novel problems in the determination of magnetic properties of organic polymers.

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