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Synthesis and Characterization of a Conjugated Polymer with Stable Radicals in the Side Groups

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ABSTRACT: The radical 2-(3,4-diethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide (**1**) was polymerized by oxidative coupling to yield poly(2-(3,4-diethynylenephenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide) (**2**) containing components of relatively low molecular weight. Different precipitation methods were used for the workup of polyradical **2**. An influence of the precipitation method on the magnetic properties was observed.

1. Introduction

Interest in purely organic magnetic materials has increased during recent years.[1−4] According to theory, organic π-conjugated polyradicals are possible candidates for molecular magnets.[5,6] Several polymers of this type have been described,[7−16] but satisfactory high-spin ordering has not yet been observed. A main problem of such investigations is the lack of reproducibility in the preparation of the products.[17] The chemical stability of most products is rather low. The theoretical viewpoints under discussion are also not fully consistent.[6]

The present paper describes the synthesis of the radical 2-(3,4-diethynylphenyl)−4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide (**1**), its polymerization to the soluble poly(2-(3,4-diethynylenephenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide) (**2**), and the influence of the precipitation method on the physical properties of the solid **2**.

Polyradical **2** contains 3,4-linked benzene rings and corresponds to a previously investigated polyradical **3** with 3,5-linked benzene rings.[15,16] The solid polymer **3** exhibited unusual magnetic properties depending on the precipitation method (evaporation of the solvent or addition of a nonsolvent). Under suitable conditions, the magnetic mass susceptibility χ_m depended on the magnetic flux density B and increased when the samples were stored at 78 K. Furthermore, $\chi_m T$ increased with decreasing T, typical for ferromagnetic interaction between unpaired electrons. As shown below, the magnetic behavior of polymers **2** and **3** differs.

2. Experimental Section

Materials. The inorganic compounds were Fluka or Merck analytical grade. 4-Bromobenzaldehyde, triphenylphosphine (from Fluka), palladium(II) acetate, ethynyltrimethylsilane (Aldrich), and 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (Eastman Kodak) were used without further purification. The solvents were Merck analytical grade. They were purified by conventional methods for use under argon.[18] The silica gel used for column chromatography (>230 mesh ASTM) was from Merck.

Instrumentation. The ^{1}H-NMR and ^{13}C-NMR spectra were measured in deuteriochloroform or in deuterated acetone (acetone-d_6) on a Bruker MSL 300 spectrometer with tetramethylsilane as standard. The mass spectra (MS) were performed on a Shimadzu Profile mass spectrometer with direct insertion (DI) of the samples and electron impact (EI) ionization (70 eV). The IR spectra were recorded on a Bomem Michelson 100 FTIR spectrometer using KBr pellets, and the UV spectra were taken from solutions in methylene chloride on a Hewlett-Packard diode array instrument 8452A in the range 240−510 nm. A Merck-Hitachi L-6000 pump was used as liquid chromatograph for GPC with methylene chloride as eluent. The absorption was recorded with a Perkin-Elmer spectrophotometer LC 55 at a wavelength of 254 nm. The polystyrene standards (M_w = 730, 11 500, 81 500, 455 000) and the columns used (PL gel 10 μm, 10^4 Å; 10 μm, 500 Å) were from Polymer Laboratories Ltd. A modified Faraday balance SUS 10, Paar AG (Graz, Austria), was used for the magnetic measurements in the range 78−300 K at magnetic flux densities of 0.42, 0.71, 1.02, and 1.32 T; freshly prepared HgCo(SCN)$_4$ was used for calibration. ESR spectra were taken on a Bruker ER 200 D X-band spectrometer; Fremy's salt ($g = 2.00550 \pm 0.00005'$) was used as reference for the determination of the g-values. Transmission electron microscopic (TEM) images were taken on a Philips 200 kV CM20/STEM.

4-Bromo-3-nitrobenzaldehyde (5). Sodium nitrate (4.86 g, 57.2 mmol) was dissolved in concentrated sulfuric acid (26.0 mL) and stirred for 20 min at 0 °C. During the addition of 4-bromobenzaldehyde (**4**) (10.00 g, 54.0 mmol), the temperature was kept below 15 °C. The solution was slowly heated to 70 °C and stirred for 60 min. After cooling to room temperature, the reaction mixture was poured into 300 mL of distilled water and stirred for 30 min. The precipitated product was filtered off and dissolved in 120 mL of chloroform. The solution was treated twice with 100 mL of sodium bicarbonate solution (5%) and three times with 100 mL of distilled water. After the solution was dried over anhydrous sodium sulfate for 12 h, it was evaporated. The crude product was purified by column chromatography using silica gel and methylene chloride to give 11.53 g of 4-bromo-3-nitrobenzaldehyde (yield 93%); ^{1}H-NMR (CDCl$_3$, ppm): 10.03 (s, 1H, −CHO), 8.31 (s, 1H, Ph), 7.95 (dd, 1H, Ph), 7.92 (dd, 1H, Ph); ^{13}C-NMR (CDCl$_3$, ppm): 188.7 (−CHO), 150.9 (C$_3$ Ph), 136.4

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(C_6 Ph), 136.2 (C_1 Ph), 132.7 (C_5 Ph), 126.2 (C_2 Ph), 121.2 (C_4 Ph); IR (KBr pellet, cm^{-1}): 3093, 3071, 2859 (ν_{CHO}), 1696 ($\nu_{C=O}$), 1594 (ν_{ph}), 1565, 1537 and 1357 ($\nu_{N=O}$), 1036 (ν_{Ph-Br}), 910, 829, 752, 718; MS (*m/z*): 229 and 231 (M^+), 228 and 230 ($M^+ - H$), 183 and 185 ($M^+ - NO_2$). Anal. Calcd for $C_7H_4BrNO_3$: C, 36.55; H, 1.75; N, 6.09. Found: C, 36.2; H, 1.8; N, 6.0.

3,4-Dibromobenzaldehyde (6). Granulated tin (16.3 g, 0.137 mol) was treated with hydrobromic acid (48%, 92.3 g) at 90 °C for 24 h to give an $SnBr_2$ solution. It was cooled to 50 °C and aldehyde **5** (10.5 g, 45.6 mmol) was added under vigorous stirring. The temperature increased to 105 °C due to the strongly exothermic reaction. After stirring for 90 min at 90 °C, the solution was cooled to 0 °C and hydrobomic acid (48%, 15.4 g) was added. A solution of sodium nitrite (3.15 g, 45.6 mmol) in 10.5 mL of distilled water was added within 30 min. During the addition the temperature was kept below 5 °C. After an additional 20 min at 0 °C, a solution of copper(I) bromide (7.44 g, 51.9 mmol) in hydrobromic acid (48%, 19.75 g) was added rapidly. The reaction mixture was heated to 100 °C and stirred for 12 h. The crude product obtained by steam distillation was dissolved in 100 mL of diethyl ether. The solution was dried over anhydrous sodium sulfate for 12 h. Then the solvent was evaporated. It was purified by column chromatography using silica gel and cyclohexane: ethyl acetate (30:1, v/v) as eluent to give 8.13 g of aldehyde **6** (yield 68%); ^{1}H-NMR ($CDCl_3$, ppm): 9.92 (s, 1H, −CHO), 8.08 (s, 1H, Ph), 7.78 (dd, 1H, Ph), 7.68 (dd, 1H, Ph); ^{13}C-NMR ($CDCl_3$, ppm): 189.8 (−CHO), 136.7 (C_1 Ph), 134.7 (C_2 Ph), 134.6 (C_5 Ph), 132.2 (C_4 Ph), 129.0 (C_6 Ph), 126.3 (C_3 Ph); IR (KBr pellet, cm^{-1}): 3086, 2829 and 2740 (ν_{CHO}), 1694 ($\nu_{C=O}$), 1575 and 1560 (ν_{Ph}), 1454, 1187, 1100, 1012 (ν_{Ph-Br}), 889 and 823; MS (*m/z*): 264 (M^+), 263 ($M^+ - H$), 235 ($M^+ - CHO$), 155 ($M^+ - CHO, Br$).

3,4-Bis((trimethylsilyl)ethynyl)benzaldehyde (7). Aldehyde **6** (1.99 g, 7.54 mmol) was dissolved in a mixture of 8 mL of toluene and 16 mL of triethylamine under argon. Palladium(II) acetate (60 mg, 0.27 mmol), triphenylphosphine (160 mg, 0.61 mmol), and copper(I) iodide (60 mg, 0.32 mmol) were added. After addition of ethynyltrimethylsilane (4.86 g, 49.5 mmol), the vigorously stirred solution was refluxed for 3 h. The mixture was cooled to room temperature and filtered. The residue of triethylamine hydrobromide was rinsed twice with 10 mL of triethylamine and dried under reduced pressure (2.74 g of triethylamine hydrobromide, 99.8%). The brown filtrate was evaporated under reduced pressure, mixed with 20 mL of sodium bicarbonate solution (5%), and extracted three times with 20 mL of methylene chloride. The combined organic fractions were dried over anhydrous sodium sulfate for 12 h and evaporated. Purification by column chromatography using silica gel and cyclohexane:ethyl acetate (15:1, v/v) as eluent gave 1.60 g of aldehyde **7** (yield 71%); ^{1}H-NMR (acetone-d_6, ppm): 10.07 (s, 1H, −CHO), 8.01 (s, 1H, Ph), 7.89 (dd, 1H, Ph), 7.71 (dd, 1H, Ph), 0.32 (s, 18H, CH_3); ^{13}C-NMR (acetone-d_6, ppm): 191.5 (−CHO), 136.8 (C_1 Ph), 134.1 (C_2 Ph), 133.7 (C_5 Ph), 131.4 (C_4 Ph), 129.1 (C_6 Ph), 127.2 (C_3 Ph), 103.2 ($Ph-C\equiv$), 100.5 ($\equiv C-Si$), 0.0 (CH_3); IR (KBr pellet, cm^{-1}): 2960, 2847 and 2718 (ν_{CHO}), 2157 ($\nu_{C\equiv C}$), 1702 ($\nu_{C=O}$), 1597 and 1550 (ν_{Ph}), 1413, 1246 (ν_{Si-C}), 1159, 1098, 948, 847 ($\nu_{Si-C bending}$), 759; MS (*m/z*): 298 (M^+), 283 ($M^+ - CH_3$). Anal. Calcd for $C_{17}H_{22}OSi_2$: C, 68.4; H, 7.5. Found: C, 68.6; H, 7.4.

2-(3,4-Diethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1oxyl 3-Oxide (1). Aldehyde **7** (304 mg, 1.02 mmol) was dissolved in a mixture of 10 mL of chloroform and 10 mL of methanol under argon. After addition of 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (370 mg, 1.50 mmol) and potassium carbonate (850 mg), the dispersion was vigorously stirred for 48 h at room temperature. An analytical amount of the dispersion was filtered and the filtrate was evaporated under reduced pressure to give crude 2-(3,4-diethynylphenyl)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine (**8**) as a solid white mass that was investigated by means of mass spectrometry without further purification. MS (*m/z*): 284 (M^+), 266 ($M^+ - OH, H$), 249 ($M^+ - 2OH, H$).

The dispersion was evaporated under reduced pressure to give a solid white mass that was dissolved in 25 mL of tetrahydrofuran. After addition of lead dioxide (1.50 g), the mixture was vigorously stirred until thin-layer chromatography showed quantitative reaction (15 min). The dispersion was filtered and the residue was twice rinsed with 20 mL of tetrahydrofuran. The dark-green/blue substance obtained by evaporation of the solution was purified by column chromatography through silica gel using methylene chloride as eluent, giving 153 mg of 2-(3,4-diethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide as dark-green/blue crystals (yield: 53.5%); IR (KBr pellet, cm^{-1}): 3250 ($\nu_{C\equiv C-H}$), 3098, 2991, 2103 ($\nu_{C\equiv C}$), 1542, 1452, 1424, 1386 (ν_{N-O}), 1354 ($\nu_{-C(CH_3)_2-}$), 1286, 1212, 1167, 1138 (ν_{N-O}), 1095, 902, 866, 846; UV (λ (ϵ), λ in nm, ϵ in $L{\cdot}mol^{-1}{\cdot}cm^{-1}$): 250 (23 748), 265 (15 071), 297 (19 866), 310 (17 530), 330 (3277), 360 (5405), 379 (11 461); MS (*m/z*): 281 (M^+), 250 ($M^+ - CH_3, O$). Anal. Calcd for $C_{17}H_{17}N_2O_2$: C, 72.6; H, 6.1; N, 10.0. Found: C, 72.3; H, 5.9; N, 9.9.

Polymerization. Monomer **1** (200 mg, 0.71 mmol) was dissolved in a mixture of 3.5 mL of pyridine and 3.5 mL of methylene chloride at 25 °C under argon, giving a dark-blue solution. After addition of copper(I) chloride (8 mg), oxygen was bubbled into the mixture for 8 h. The color of the solution changed to dark-green after a reaction time of 10 min. The reaction mixture was filtered and poured into 120 mL of *n*-hexane to give a precipitate which was filtered off and redissolved in a mixture of 3.5 mL of pyridine and 3.5 mL of methylene chloride. The dark-green solution was divided into two parts of approximately equal volume.

The first part was poured into 60 mL of *n*-hexane. The precipitate was filtered off, washed twice with 10 mL of *n*-hexane, and dried under a stream of argon and then in vacuo, giving 88 mg of polymer **2** as a green powder (sample A).

The second part was slowly evaporated under a stream of argon and then dried in vacuo, giving 91 mg of polymer **2** as a dark-green film (sample B).

Total yield of samples A + B: 90.5%; IR (KBr pellet, cm^{-1}): 2924, 2853, 2213 and 2145 ($\nu_{C\equiv C}$), 1674, 1649, 1535, 1387 (ν_{N-O}), 1366 ($\nu_{-C(CH_3)_2-}$), 1140 (ν_{N-O}), 837, 734. UV (λ (ϵ), λ in nm, ϵ in $L{\cdot}mol^{-1}{\cdot}cm^{-1}$, calculated on the repeating unit of the polymer): 283 (15 555), 334 (19 966), 352 (20 965), 391 (11 598), 405 (8722).

3. Results and Discussion

Synthesis. The monomer **1** was synthesized *via* Scheme 1. 4-Bromobenzaldehyde (**4**) was converted to 4-bromo-3-nitrobenzaldehyde (**5**) by reaction with a mixture of concentrated sulfuric acid and sodium nitrate, a reaction already used for the preparation of 4-chloro-3-nitrobenzaldehyde.[19] 3,4-Dibromobenzaldehyde (**6**) was prepared by a Sandmeyer reaction.[20] The reaction of aromatic bromides with ethynyltrimethylsilane, using palladium(0) generated *in situ* as catalyst,[21,22] was applied for the conversion of aldehyde **6** to 3,4-bis((trimethylsilyl)ethynyl)benzaldehyde (**7**). The reaction needed an unusually high excess of ethynyltrimethylsilane and was not satisfactory without the addition of copper(I) iodide. Incomplete reaction gave mixtures of aldehyde **7** and bromo((trimethylsilyl)ethynyl)benzaldehydes. Compound **7** was converted to monomer **1** in a "single-step" reaction[22] that was previously used for the preparation of 2-(3,5-diethynylenephenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide, the monomer for the preparation of polymer **3**. Reaction of the aldehyde group of **7** with 2,3-bis(hydroxyamino)-2,3-dimethylbutane, prepared *in situ* by reaction of 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate with potassium carbonate, and simultaneous cleavage of the $\equiv C-Si-$ bonds due to the alkaline medium gave imidazolidine **8**, which was oxidized with lead dioxide to monomer **1**. It was not possible to isolate imidazolidine **8** in high purity by recrystallization, sublimation, or column chromatogra-

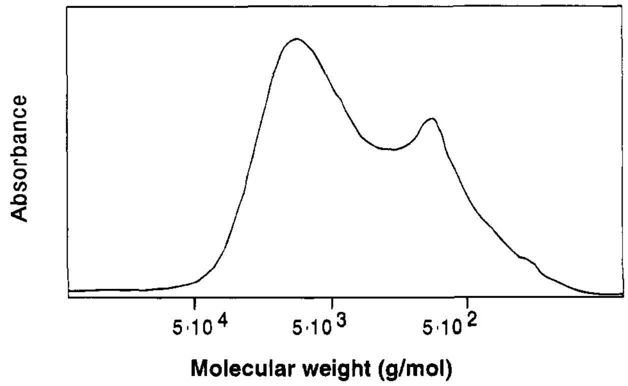
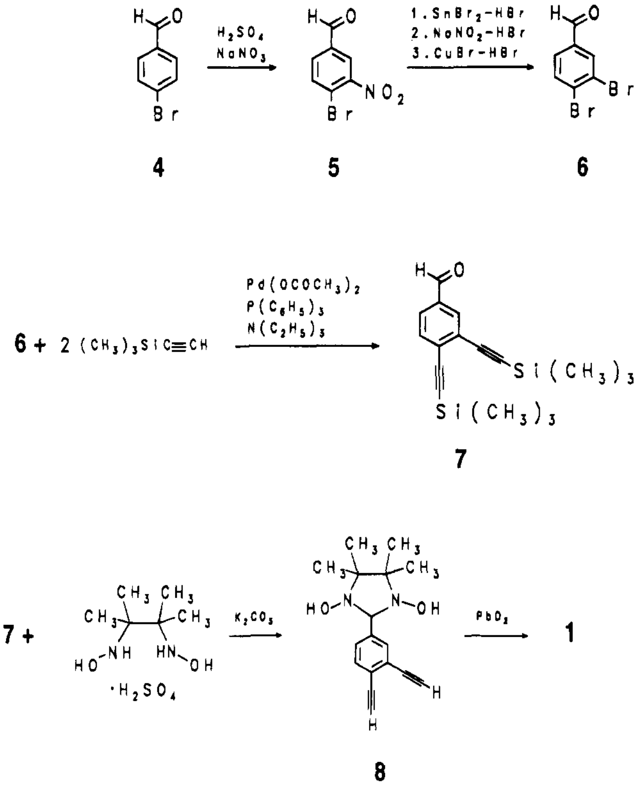


Figure 1. Molecular weight distribution of polymer **2**.

Scheme 1



phy. The structure could be analyzed by investigating the crude product using mass spectrometry (see Experimental Section).

The oxidative coupling of the terminal ethynyl groups of monomer **1** with Cu_2Cl_2/O_2, a common reaction for the preparation of poly(diacetylenes),[13-16,23,24] was used for the preparation of polymer **2**. The samples A and B of polymer **2** were prepared by different precipitation methods of solutions of polymer **2** in a mixture of methylene chloride and pyridine (see Experimental Section).

Characterization. The molecular weight distribution of polymer **2** which was obtained by GPC had two maxima; see Figure 1. The first maximum was approximately 8930 g/mol. This corresponds to a polymerization degree of 32 monomeric units, indicating successful coupling of monomer **1**. The molecular weight of the second maximum was approximately 850 g/mol and assigned to the formation of a trimer; the cyclotrimer, $(C_{17}H_{15}N_2O_2)_3$, has $M = 837.95$ g/mol.

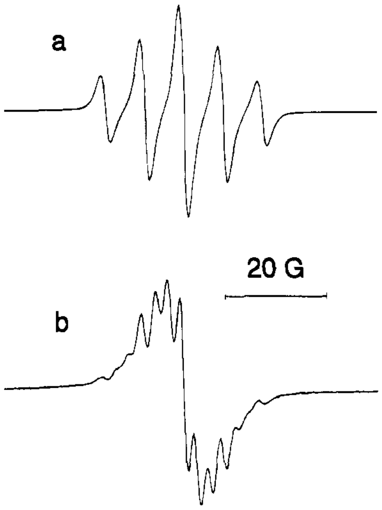


Figure 2. ESR spectra: (a) monomer **1** ($c = 0.141$ mmol/L); (b) polymer **2** ($c = 0.139$ mmol/L, calculated on the repeating unit of the polymer).

Attempts to separate polymer **2** from small oligomers by reprecipitation with various solvents and nonsolvents were not successful. The polymerization was optimized to prepare a product with smaller fractions of trimers. The method described in the Experimental Section gave the most satisfactory results. The fraction of trimers was estimated to contain approximately 10–15% of the monomer units.

The IR spectrum of polymer **2** showed the typical absorptions of nitronyl nitroxides at 1387 and 1140 cm^{-1}.[22] This ensures that the polymerization proceeded without decomposition of the radical centers. The absorption of monomer **1** at 3250 cm^{-1}, characteristic of the terminal ethynyl groups, disappeared. Additional peaks at 2213 and 2145 cm^{-1} are assigned to the substituted $-C{\equiv}C-$ bond.

The UV spectra of polymer **2** showed a broad absorption from 240 to 480 nm with maxima at 352, 391, and 405 nm.

The ESR spectra of monomer **1** and polymer **2** dissolved in methylene chloride are reproduced in Figure 2. Monomer **1** showed a $2nI + 1$ pattern ($I = 1$, $n = 2$) due to two equivalent nitrogen atoms (Figure 2a). The g-value determined is 2.00600 ± 0.00005 and the hyperfine coupling constant $a_N = 7.53 \pm 0.06$ G, typical values for a nitronyl nitroxide substituted with a phenyl group in position 2.[22] Polymer **2** showed a broad signal in the $\Delta m_s = \pm 1$ region with a g-value of 2.00600 ± 0.00005 and a coupling constant of $a = 2.5 \pm 0.06$ G (Figure 2b). The intense absorptions in the spectrum indicate a high spin concentration.

TEM images showed different morphologies for samples A and B; see Figure 3. This could be a reason for ordering phenomena leading to the different magnetic properties of samples A and B.

Magnetic Properties. The magnetic mass susceptibilities of monomer **1** and polymer **2** were measured at 78–300 K. For diamagnetic correction we tried to isolate pure imidazolidine **8**, without success. Thus, the diamagnetic mass susceptibility of 2-(3,5-diethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide (χ_{dia} -7.55×10^{-9} m^3/kg),[15] a compound with very similar chemical structure, was applied. $\chi_m T$ of monomer **1** was a linear function of the temperature T and did not depend on the magnetic flux density used during measurement. No deviations from Curie's law (eq 1, the paramagnetic Curie temperature $\Theta = 0$ K) were observed.

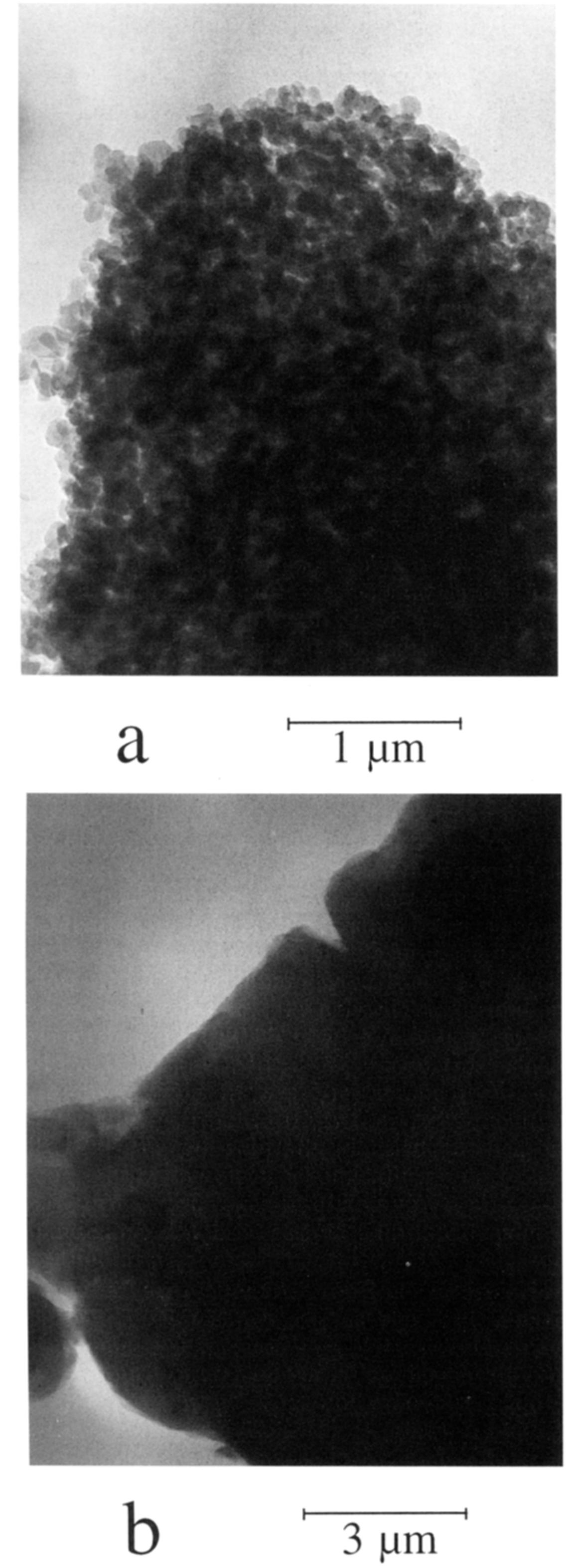


Figure 3. TEM images of sample A (a) and sample B (b).

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

The Curie constant C_{exp} was 1.66×10^{-5} m^3 K/kg. Calculation of the theoretical value for ideal paramagnetic behavior (eq 2; $S = {}^1/_2$, $M = 281.33$ g/mol, and $g = 2.0060$ as an approximation; the other symbols have their usual meanings) gave $C_{theor} = 1.68 \times 10^{-5}$ m^3 K/kg.

$$C_{theor} = N_A g^2 \mu_0 \mu_B{}^2 S(S + 1)/3Mk \qquad (2)$$

The magnetic properties of polymer **2**, samples A and B, did not depend on the magnetic flux density.

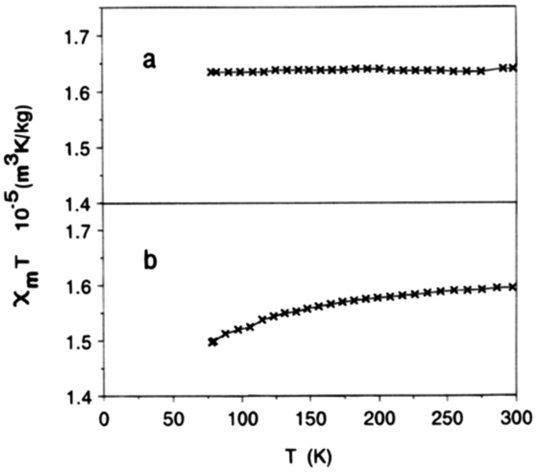
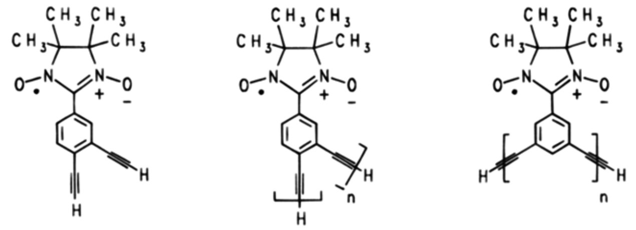


Figure 4. $\chi_m T$ as a function of the temperature T for polymer **2**: (a) sample A; (b) sample B.

Chart 1



1 **2** **3**

Results for sample A are shown in Figure 4a. $\chi_m T$ was a linear function of T. No positive or negative deviations from the $\chi_m T$ vs T plot indicating ferro- or antiferromagnetism were observed. The Curie constant was $C_{exp} = 1.64 \times 10^{-5}$ m^3 K/kg. The theoretical value is $C_{theor} = 1.69 \times 10^{-5}$ m^3 K/kg, calculated with $S = {}^1/_2$, $g = 2.0066$, and $M = 279.31$ g/mol (repeating unit of the polymer) according to eq 2.

The magnetic properties of polymer **2**, sample B, are given in Figure 4b. $\chi_m T$ was not a linear function of T. The negative deviation of the $\chi_m T$ vs T plot means an antiferromagnetic interaction between unpaired electrons. The Curie constant $C_{exp} = 1.63 \times 10^{-5}$ m^3 K/kg was reproducible in several experiments. The paramagnetic Curie temperature was $\Theta = -6.9$ K, but not very reproducible. By extrapolation, all experiments gave negative values of Θ between -4.2 and -11 K. Only these samples of polymer **2** exhibited antiferromagnetic properties. Thus, the precipitation method seems to be a critical parameter for the magnetic properties. In contrast, polymer **3**, described previously, exhibited weak ferromagnetic interactions of unpaired electrons.[15,16] This difference is probably caused by the changed structure of the conjugated backbone.

4. Conclusions

The main result of this investigation is that the magnetic properties of polyradical **2** are influenced by the precipitation method. In our opinion, future search for purely organic macromolecular magnets should focus not only on the synthesis and characterization of new polyradicals but also on the development of suitable precipitation methods.

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