Paramagnetic conjugated polymers with stable radicals in side groups

Robert Saf[1], Klaus Hummel[1,*], Karl Gatterer[2], and Harald P. Fritzer[2]

[1]Institut für Chemische Technologie organischer Stoffe, Technische Universität Graz, Stremayrgasse 16, A-8010 Graz, Austria
[2]Institut für Physikalische und Theoretische Chemie, Technische Universität Graz, Rechbauerstrasse 12, A-8010 Graz, Austria
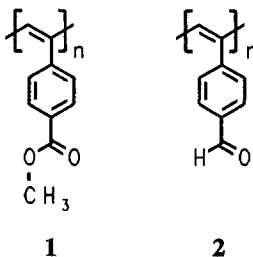
Summary

Poly(1,3-dihydroxy-2-(4-ethynylphenyl)-4,4,5,5-tetramethylimidazolidine), poly(2-(4-ethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-oxide), poly(4-(4-ethynylbenzylideneamino)-2,2,6,6-tetramethylpiperidine) and poly(4-(4-ethynylben-zylideneamino)-2,2,6,6-tetramethylpiperidine-1-oxyl) were prepared from poly(4-ethynyl-benzaldehyde). The products were characterized spectroscopically (IR, UV, ^{1}H and ^{13}C NMR) and with respect to the magnetic susceptibility. The polyradicals (1-oxyl compounds) showed paramagnetic properties obeying Curie's law.

Introduction

Several attempts have been made to obtain purely organic macromolecular materials exhibiting paramagnetic or ferromagnetic properties (1-3). Ferromagnetism was observed only in rare cases to a low percentage mainly at low temperatures (4-6).

Within a program to prepare polymers with special magnetic properties, we synthesized substituted poly(acetylenes). Poly(methyl-4-ethynylbenzoate) (**1**) was reduced with LiAlH(OCH$_3$)$_3$ and the product was oxidized with dimethyl sulfoxide / oxalyl chloride to poly(4-ethynylbenzaldehyde) (**2**).


1   **2**

As shown in Eq. (1), the reaction of polymer **2** with 2,3-dimethyl-2,3-butanediyldi-hydroxylamine (**3**) gave poly(1,3-dihydroxy-2-(4-ethynylphenyl)-4,4,5,5-tetramethylimid-azolidine) (**4**). This was oxidized to poly(2-(4-ethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihy-dro-1H-imidazol-1-oxyl-3-oxide) (**5**), a nitronyl nitroxide.
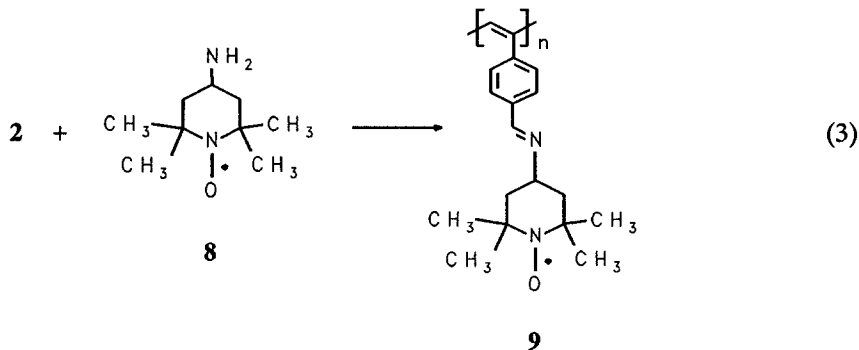
---

*Corresponding author

$$(1)$$
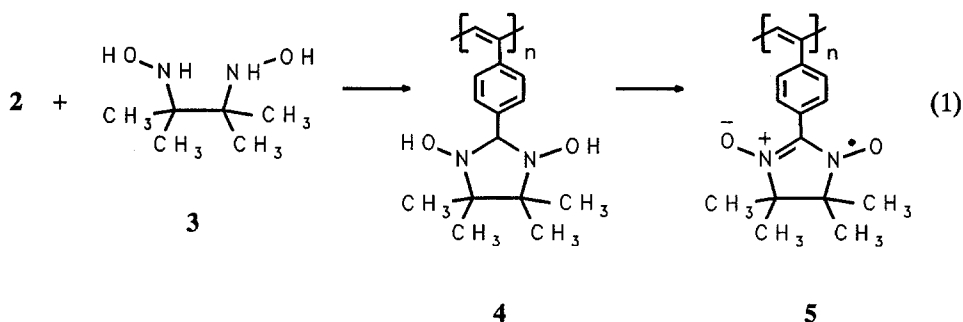
With 4-amino-2,2,6,6-tetramethylpiperidine (**6**), the resulting polymer was poly(4-(4-ethynylbenzylideneamino)-2,2,6,6-tetramethylpiperidine) (**7**), see Eq. (2).


$$(2)$$
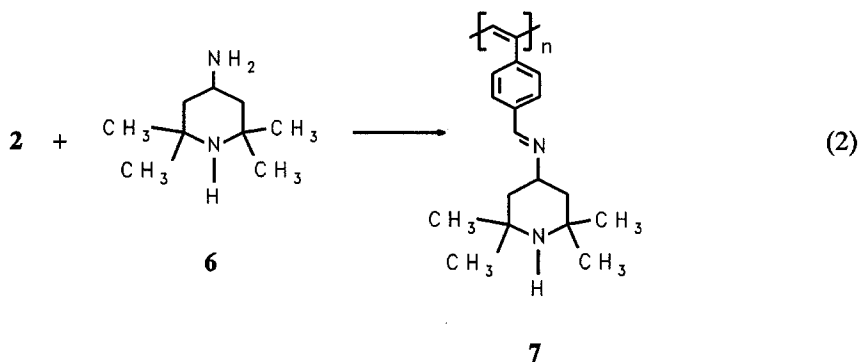
Correspondingly, the reaction of **2** with 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (**8**), Eq. (3), gave the product poly(4-(4-ethynylbenzylideneamino)-2,2,6,6-tetramethyl-piperidine-1-oxyl) (**9**).

$$(3)$$

The reaction of low-molecular-weight aldehydes with **3** to imidazolidines and the oxidation to the corresponding nitronyl nitroxides have already been reported by Ull-

mann et al. (7). Nitronyl nitroxides were employed to prepare low-molecular-weight ferromagnetic products (5,8) and precursors of polyradicals (9). The reaction of aromatic aldehydes with **8** was previously used for the preparation of liquid crystalline nitroxides (10). The polyradicals **5** and **9** are examples of poly(acetylenes) **10** with substituents R having a radical centre. Only a few polymers with this structure have as yet been synthesized (11-13). Theoretical calculations suggest that such polymers permit interaction of the radicals through the π-electron system (14-16). This could lead to superparamagnetic or ferromagnetic properties.

10
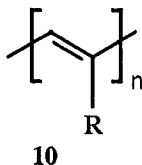
The polyradical **5** was compared with polymer **4**, and the polyradical **9** with polymer **7** by means of IR and UV spectroscopy. The ^{1}H and ^{13}C NMR spectra of polymers **4** and **7** were recorded. An investigation of the ESR spectra of polymers **5** and **9** will be published later (17). Magnetic measurements show that the polyradicals **5** and **9** are paramagnetic.

Experimental

General
All reactions were carried out under dry argon. The solvents benzene, chloroform, n-pentane, tetrahydrofuran (THF) and toluene were distilled from sodium before use. Dimethylformamide (DMF) was dried over $MgSO_4$ followed by distillation under reduced pressure. Methanol was dried with magnesium before distillation. The polyradicals **5** and **9** were stored under argon until the magnetic properties were examined.

Starting materials
Poly(4-ethynylbenzaldehyde) (**2**) was prepared according to Iwamura (18) by reduction of poly(methyl-4-ethynylbenzoate) (**1**) with $LiAlH(OCH_3)_3$ followed by oxidation with dimethyl sulfoxide / oxalyl chloride at -30 °C (-60 °C in (18)). According to ^{13}C NMR and IR spectra the purity of polymer **2** was higher than 98 %. — 2,3-Dimethyl-2,3-butanediyldihydroxylamine (**3**) was prepared from 2,3-dimethyl-2,3-dinitrobutane (Aldrich Chemical Co.) as described by Lamchen and Mittag (19). 4-Amino-2,2,6,6-tetramethylpiperidine (**6**) and 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (**8**) (both from Aldrich Chemical Co.) were used without further purification.

General procedure for the preparation of the polymers 4, 7 and 9
200 mg (1.54 mmol of repeat units) of polymer **2** were soaked in 5 ml of chloroform. The dispersion was stirred at 40 °C for 1 h. A solution of 2.0 mmol of **3**, **6** or **8** in 5 ml of chloroform was added. The polymer was completely dissolved within 15 min. The mixture was concentrated by evaporation of the solvent to a volume of 5 ml. The dark-red solution was stirred for additional 2 h and then heated to reflux for 20 h. The water resulting from the condensation reaction was continuously removed with K_2CO_3 using a

Dean-Stark water separator (20). After cooling to room temperature, the polymers were precipitated by pouring the solution into 20 ml of n-pentane. They were reprecipitated by dissolving in 4 ml of THF and pouring into 20 ml of n-pentane. Yields: 4: 312.4 mg (78.1 %); 7: 289,7 mg (70.2 %); 9: 332.1 mg (76.3 %).

In a series of experiments, other solvents were tried for the reaction between the polymer 2 and the dihydroxylamine 3. The conversion was checked by IR spectroscopy. Methanol or benzene proved to be unsatisfactory. The use of a mixture of DMF and toluene led to side reactions; dimethylamine resulting from the decomposition of DMF (21) reacted with 2.

Preparation of polyradical 5

To a solution of 65 mg (0.25 mmol of repeat units) of polymer 4 in 10 ml of THF was added 0.4 g of lead dioxide. The dispersion was stirred at 25 °C for 3 h. Then the lead oxides were filtered off. The polymer was precipitated by pouring the solution into 25 ml of n-pentane. Reprecipitation by dissolving in 3 ml of THF and pouring into 15 ml of n-pentane yielded 52 mg (80.6 %) of a dark-red polymer.

Instrumental equipment

NMR spectra were measured in $CDCl_3$ on a Bruker MSL 300 spectrometer with $Si(CH_3)_4$ as standard. IR spectra were recorded on a Bomem Michelson 100 FTIR spectrometer using films of the polymers on NaCl; a KBr cell, pathlength 0.025 mm, was applied to liquid samples. UV spectra were taken from solutions in THF on a Hewlett Packard diode array instrument 8452A (190 to 510 nm). The magnetic susceptibility was measured on a modified Faraday balance SUS 10, Paar AG (Graz, Austria); calibration was carried out with freshly prepared $HgCo(SCN)_4$. A Perkin Elmer Series 10 instrument was used as liquid chromatograph for GPC. The absorption was recorded with a Perkin Elmer spectrophotometer LC 55 at a wavelength of 254 nm. The columns used (PL gel 10 μ, 10^5 Å; 5 μ, 10^3 Å; 5 μ, 10^2 Å) and the polystyrene standards (M_w = 730, 11500, 81500, 455000, 1560000) were from Polymer Lab. Ltd..

Results and discussion

Molar mass M of the products

The molar mass distribution of poly(methyl-4-ethynylbenzoate) (1) was investigated by means of GPC; the calibration was carried out with polystyrene standards. The maximum of the mass distribution was ca. M = $1.5 \cdot 10^5$. This corresponded to Iwamura et al. (18). The non-radical polymers 4 and 7 had a higher maximum at M = $1.8 \cdot 10^5$ for 4 and $2.0 \cdot 10^5$ for 7. Polymer 2 was only partly soluble, perhaps because of interaction with the solvent and intramolecular interactions (18).

IR and UV spectra of polymers 4 and 5

The IR spectra of polymer 4 and the corresponding polyradical 5 are shown in Fig. 1. For 4, the disappearance of the CO absorption at 1697 cm^{-1} and the appearance of the OH group at 3250 cm^{-1} confirm that most of the aldehyde groups of the parent polymer 2 reacted. The spectrum of polyradical 5 shows absorptions near 1140 cm^{-1} and 1370 cm^{-1} (N-O stretching frequency) which are typical for nitronyl nitroxides (7,20). There is a stronger absorption at 1147 cm^{-1} for polymer 5 compared with the absorption

at 1167 cm^{-1} for **4**. Polyradical **5** has an additional band at 1600 cm^{-1}. The absorption at 3250 cm^{-1} is greatly decreased. This indicates oxidation of the OH groups in polymer **4**.

The UV extinctions ϵ are given here in $l \cdot mol^{-1} \cdot cm^{-1}$. The spectrum of polymer **4** in THF with broad absorption from 212 nm ($\epsilon = 12013$) to 500 nm ($\epsilon = 554$) is typical for conjugated polymers. The spectrum of polyradical **5** in THF changed depending on the time between dissolution and the recording of the spectrum. About 15 min after dissolution the typical absorption at 370 nm was observed only with small intensity ($\epsilon = 3471$). In addition, the spectrum showed a broad absorption from 212 nm ($\epsilon = 11442$) to 500 nm ($\epsilon = 765$) with a maximum at 244 nm ($\epsilon = 12002$). 24 h after dissolution, the spectrum displayed a significantly stronger absorption at 370 nm ($\epsilon = 5551$); the absorption extended from 210 nm ($\epsilon = 5506$) to 500 nm ($\epsilon = 909$) with maxima at 237 nm ($\epsilon = 12012$), 267 nm ($\epsilon = 9776$) and 274 nm ($\epsilon = 10224$).
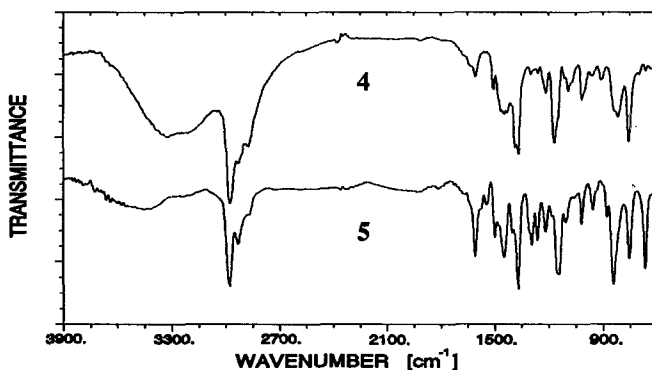

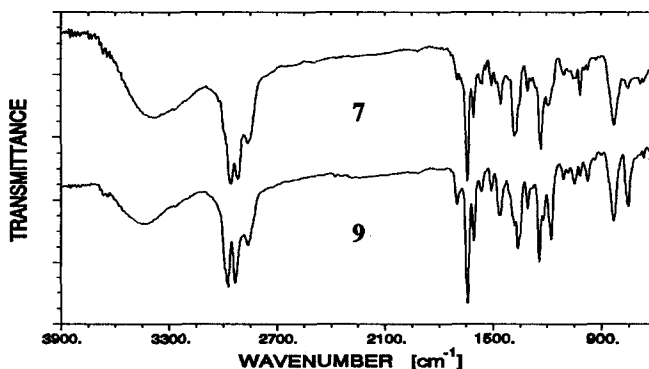Fig. 1. FTIR spectra of polymers **4** and **5**

Fig. 2. FTIR spectra of polymers **7** and **9**

IR and UV spectra of polymers 7 and 9

The IR spectra of polymer 7 and polyradical 9 of similar structure are reproduced in Fig. 2. Polyradical 9 has significant additional absorptions at 1459, 1358, 1241 and 1173 cm^{-1}. These differences can also be seen in the IR spectra of 6 and 8 (22).

The UV spectrum of polymer 7 shows broad absorption from 213 nm (ϵ = 13433) to 500 nm (ϵ = 523) with a strong maximum at 260 nm (ϵ = 11144). The UV spectrum of 9 also shows broad absorption. The intensity is higher, for example at 213 nm (ϵ = 16760), 260 nm (ϵ = 13953) and 500 nm (ϵ = 595).

NMR spectra of polymers 4 and 7

The characteristic signals of the ^{1}H and ^{13}C NMR spectra of the polymers 4 and 7 are listed in Table 1.

Table 1. ^{1}H and ^{13}C NMR spectra of polymers 4 and 7 in CDCl$_3$; δ in ppm

4		7	
^{1}H	^{13}C	^{1}H	^{13}C
2.2 (12H)	15-33 (CH$_3$)	0.5-1.8 (17H)	28-30 (CH$_3$)
4.1-5.0 (1H)	78-82 (CH)	1.9-2.4 (1H)	35-37 (CH$_2$)
5.5-8.7 (7H)	58-68 (C$_3$CN)	3.4-3.9 (1H)	45-51 (C$_2$CHN)
	120-148 aromatic, vinyl	6.0-8.6 (5H)	62-64 (C$_3$CN)
			125-145 aromatic, vinyl
			158-160 (CH=N)

Magnetic properties

The magnetic susceptibility of the polymers was measured in the thermal range 77 to 300 K at magnetic flux densities of 0.42, 0.71, 1.02 and 1.32 Tesla; the results did not depend on the flux density. The values of the diamagnetic susceptibility (in m^3/kg) were -5.93 · 10^{-9} for polymer 4 and -6,79 · 10^{-9} for polymer 7. These values were used for the diamagnetic correction in the determination of the paramagnetic susceptibility χ_m of the polyradicals 5 and 9. Fig. 3 demonstrates that 1/χ_m is a linear function of the temperature T for these polyradicals; the extrapolation of the straight lines shows that 1/χ_m is zero for T = 0 K (Curie's law). No deviations indicating ferro- or antiferromagnetic interactions or other more ordered spin states were observed.
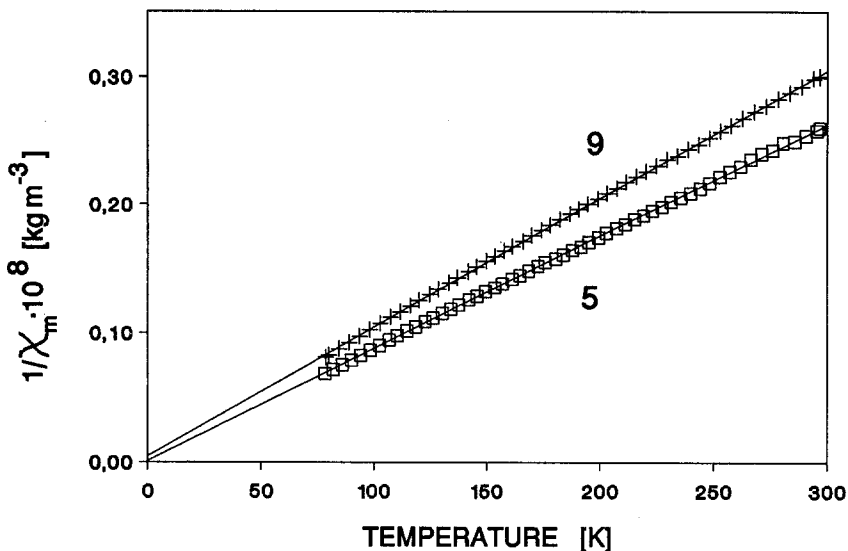
Fig. 3. Plot of $1/\chi_m$ against temperature for the polymers **5** and **9**

Chemical Abstracts Registry No.
1, 115859-42-2; **2**, 115859-44-4; **3**, 14384-45-3; **6**, 36768-62-4; **8**, 14691-88-4;

References
1. A.L. Buchachenko, Mol. Cryst. Liq. Cryst. **176**, 307 (1989), and references therein.
2. L. Dulog, Nachr. Chem. Tech. Lab. **38**, 445 (1990), and references therein.
3. D.A. Dougherty, D.A. Kaisaki, Mol. Cryst. Liq. Cryst. **183**, 71 (1990), and references therein.
4. A.A. Ovchinnikov, V.N. Spector, Synth. Met. **27**, B615 (1988).
5. K. Awaga, Y. Maruyama, Chem. Phys. Lett. **158**, 556 (1989).
6. H. Tanaka, K. Tokuyama, T. Sato, T. Ota, Chem. Lett. 1813 (1990).
7. E.F. Ullmann, J.H. Osiecki, D.G.B. Boocock, R. Darcy, J. Am. Chem. Soc. **94**, 7049 (1972).

8. Y. Nakamura, N. Koga, H. Iwamura, Chem. Lett. 69 (1991).
9. L. Dulog, J.S. Kim, Makromol. Chem. **190**, 2609 (1989).
10. A.T. Pudzianowski, A.E. Stillman, R.N. Schwartz, B.L. Bales, E.S. Lesin, Mol. Cryst. Liq. Cryst. **34**, 33 (1976).
11. H. Nishide, N. Yoshioka, T. Kaneko, E. Tsuchida, Macromolecules **23**, 4487 (1990).
12. E.J. Vliestra, R.J.M. Nolte, J.W. Zwikker, W. Drenth, E.W. Meijer, Macromolecules **23**, 946 (1990).
13. H. Iwamura, N. Ishida, Jpn. Kokai Tokkyo Koho 35 (1991).
14. A.A. Ovchinnikov, Theor. Chim. Acta **47**, 297 (1978).
15. N.N. Tyutyulkov, S.H. Karabunarliev, Chem. Phys. **112**, 293 (1987).
16. P.M. Lahti, A.S. Ichimura, J. Org. Chem. **56**, 3030 (1991).
17. R. Saf , K. Hummel, in preparation.
18. H. Iwamura, R.D. McKelvey, Macromolecules **21**, 3386 (1988).
19. M. Lamchen, T.W. Mittag, J. Chem. Soc. C, 2300 (1966).
20. J.F.W. Keana, Spin Labeling in Pharmacology, 1 (1984).
21. D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford - Frankfurt 1980.
22. C.J. Pouchert, The Aldrich Library of Infrared Spectra, Edition III, 1981.