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Synthesis and Characterization of a Stable Poly(iminomethylene) with Pendant Phenoxyl Radicals

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Polymer **1b**, $[R-N=C<]_n$, where R is 4-oxyl-3,5-diphenylphenyl, has been synthesized by oxidation of polymer 8 (R = 4-hydroxy-3,5-diphenylphenyl). The latter is prepared by the $NiCl_2$-catalyzed polymerization of the corresponding isocyanide. Magnetic susceptibility measurements indicate no evidence for ferromagnetism or any other short-range ordering among unpaired spins in the temperature region 77–320 K. A spin density of 0.8 spin/repeating unit is measured. ESR spectroscopy indicates that **1b** is a paramagnet at both 4 and 320 K.

Introduction

Since their discovery in the nineteenth century, it is known that isocyanides easily polymerize. Comprehensive studies of this polymerization have been performed by Millich[1–4] and by Yamamoto and other Japanese workers.[5,6] A large variety of isocyanides have been polymerized by our group, applying nickel(II) salts as catalysts.[7–10]

Polymers of isocyanides, more systematically called poly(iminomethylenes) or poly(carbonimidoyls), are rigid rods with a helical configuration; there are approximately four $R-N=C<$ units per helical turn.[1–4,11] Figure 1 gives a top view of a right-handed poly(iminomethylene) in its most stable all-anti configuration. Syn–anti isomerization, however, cannot be excluded.[12] Each molecule has four stacks of groups R parallel to the helical axis. An orderly stacking is experimentally supported by the observation of ion conductivity by polymers with pendant crown ether groups. The ions probably flow through channels formed by crown ether stacks.[13]

Recently, we prepared polymers of isocyanides with pendant piperidyl-*N*-oxyl groups **1a** with the aim of obtaining ferro- or antiferromagnetic interactions of the pending stable radicals, due to the perfect alignment of the stacks.[14] Despite this stacking, polymer **1a** is paramagnetic with approximately 0.7 spin/repeating unit. No ordering among unpaired spins has been found.

Polymers substituted with stable radicals figure prominently in current research on possible ferromagnetic properties.[15–21] A polymer of (3,5-di-*tert*-butyl-4-hydroxyphenyl)acetylene has been synthesized by Tsuchida et al.[15] and oxidized to the corresponding polyphenoxyl compound. The latter was paramagnetic with a limited concentration of unpaired spins of approximately 0.1 spin/repeating unit.

In a subsequent step in our research on polyradicals, we synthesized and characterized a polymer of an isocyanide with pendant phenoxyl radicals. These phenoxyl radicals are thought to have a spin density distributed over the aromatic ring. Hence, we anticipated a higher effect of ordering among the unpaired spins in the polymer with phenoxyl radical units, **1b**, than with the polymer with nitroxyl radical units, **1a**.

Experimental Section

Instrumentation. Nuclear magnetic resonance spectra are recorded on a Varian EM 360A and a VXR 400S instruments at 60 and 400 MHz for ^1H and on a Varian VXR 400S instrument at 100 MHz for ^{13}C; the chemical shifts are reported in ppm downfield from TMS for ^1H and ^{13}C. The ^{13}C spectra are obtained with ^1H broadband decoupling, and the chemical shifts are assigned by comparison with the calculated chemical shifts and by considering the intensities of the peaks. Infrared data are obtained from a Perkin-Elmer 283 spectrophotometer. Viscosity is measured at 30 °C in THF, in an Ubbelohde viscometer. Size-exclusion chromatography is carried out with two columns: Polymer Laboratories and Plgel 10μ. A Roth Scientific Ltd. Viscotek differential refractometer/viscometer detector at 35 °C is used. The columns are calibrated with polystyrene and poly(methyl methacrylate) standards, and THF is used as an eluent. Melting points are uncorrected and obtained from a Mettler FP5 and FP51

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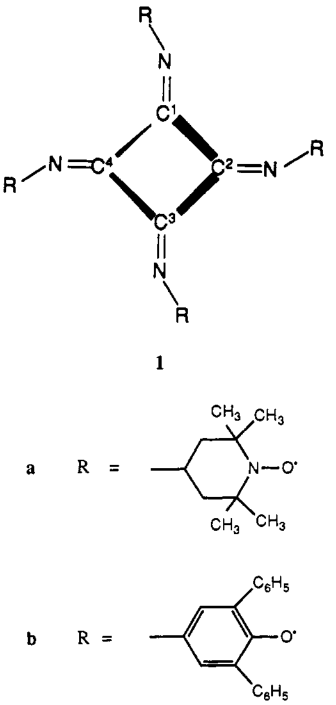


Figure 1. Top view of right-handed polymer molecule.

capillary melting point apparatus. ESR and magnetic susceptibility instrumentation is as in ref 14. Elemental analyses are performed by the Elemental Analytical Section of the Institute for Applied Chemistry TNO, Zeist, The Netherlands, and by the Microanalysis Group, Department of Chemistry, University of Durham, Durham, UK. EI and CI MS are performed on a 7070 E VG analytical mass spectrometer.

Materials. Most compounds are from Janssen and used without further purification. All solvents are distilled prior to use and dried if noted.

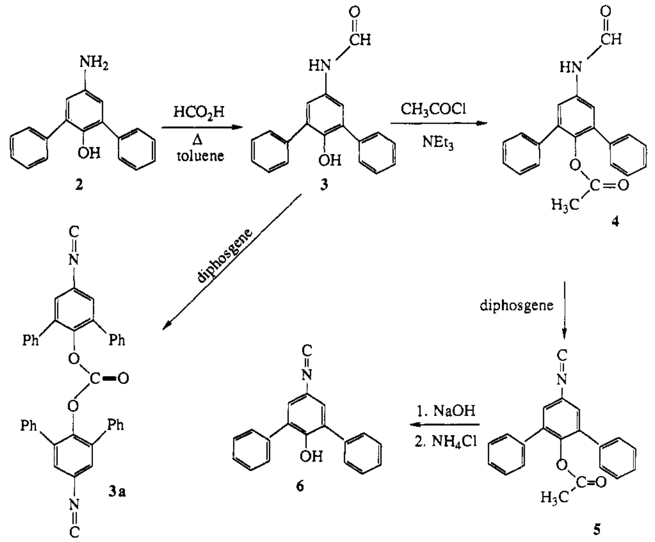
4-(*N*-Formylamino)-2,6-diphenylphenol (3). In a 250-cm^3 round-bottomed flask equipped with a magnetic bar, a condenser, and a Dean-Stark trap are mixed at room temperature 4-amino-2,6-diphenylphenol (12.35 g, 47 mmol) and concentrated formic acid (98–100%, 50 cm^3) with stirring. Toluene (dry, 160 cm^3) is added; the mixture is protected with a blanket of N_2, and the vessel is placed in an oil bath. Stirring is continued, and the bath temperature is raised to 110–120 °C. The excess acid and the water formed are removed by distillation. Heating is continued for 12 h; then the volume of toluene is reduced to 50 cm^3. The formamide crystallizes at room temperature (powder). It is filtered and washed first with small portions of toluene, followed by water, a solution of sodium hydrogen carbonate and water, and finally toluene. It is dried in a desiccator in the presence of phosphorus pentoxide under full vacuum; yield 11.51 g (85%), mp 167–168 °C. ^{1}H NMR ($CDCl_3$–DMSO-d_6) δ 6.98 (s, 2 H, CH ortho to N–CO), 7.2–7.65 (m, 10 H, phenyl), 8.2 (m, 1 H, COH), 9.62 (b, 1 H, NH); ^{13}C NMR (DMSO-d_6), two isomers (the first cited shift corresponds to the predominant isomer and the second one to the minor isomer) δ 121.03 and 119.81 (C ortho to N—C=O), 127.21 and 127.26 (C^4 of Ph), 128.39 and 128.35 (C^2 and C^6 of Ph), 129.46 and 129.55 (C^3 and C^5 of Ph), 131.52 and 132.22 (C meta to N—C=O), 131.59 and 131.46 (arom C attached to N), 138.72 and 138.49 (C^1 of Ph), 146.69 and 147.16 (C para to N—C=O), 159.46 and 162.98 (C=O); IR (KBr) 3280 (s, NH), 3300–2500 (b, OH), 3045 (m, CH), 1655 and 1535 (s, NCO), 1595 and 1570 cm^{-1} (m, phenyl). Anal. Calcd. for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.05; H, 5.18; N, 4.52. EI and CI MS calcd for $C_{19}H_{15}NO_2$ 289.34, found (M^+) 289 and ($M + NH_4^+$) 307.

4-(*N*-Formylamino)-2,6-diphenylphenyl Acetate (4). A mixture of formamide **3** (1.447 g, 5.02 mmol), triethylamine (0.7 cm^3, 5.05 mmol) and dichloromethane (dry, 100 cm^3) is placed in a round-bottomed flask (250 cm^3) equipped with an addition funnel and a guard tube of $CaCl_2$. The heterogeneous mixture is cooled with an ice bath, and a solution of acetyl chloride (0.36 cm^3, 6.37 mmol) in 5 cm^3 of dichloromethane is added through the addition funnel dropwise with magnetic stirring over 20 min. The clear solution is stirred for another 3 h at ambient temperature. The organic layer is washed twice with 30 cm^3 of water, then dried over a 4A molecular sieve. The solvent is rotaevaporated to leave a solid, which is dried again in a desiccator in the presence of P_2O_5 under full vacuum; yield 1.342 g (81%), mp 72–75 °C. ^{1}H NMR ($CDCl_3$, 400 MHz), two isomers, δ 1.782 and 1.784 (s, 3 H, CH_3), 7.08 and 7.53 (s, 2 H, arom ortho to N—C=O), 7.36–7.42 (m, 10 H, Ph), 8.02 and 8.69 (br, 1 H, NH), 8.2 and 8.67 (d, 1 H, H—C=O); ^{13}C NMR ($CDCl_3$), two isomers (the first cited shift corresponds to the predominant isomer, the second one to the minor isomer) δ 20.45 and 20.34 (CH_3), 121.35 and 120.11 (C ortho to N—C=O), 127.67 and 127.94 (C^4 of Ph), 128.25 and 128.37 (C^2 and C^6 of Ph), 128.78 and 128.69 (C^3 and C^5 of Ph), 135.16 and 134.88 (arom C attached to N—C=O), 136.25 and 136.74 (C meta to N—C=O), 137.09 and 137.23 (C^1 of Ph), 141.30 and 142.22 (C para to N—C=O), 159.29 and 162.66 (N—C=O), 169.46 and 169.18 (O—C=O); IR (KBr) 3280 (br, NH), 3040 (m, CH), 1752 (s, CO–CH_3), 1680 and 1535 (s, CO–NH), 1585 (m, Ph), 1565 (w, Ph) cm^{-1}. Anal. Calcd for $C_{21}H_{17}NO_3$: C, 76.12; H, 5.17; N, 4.23. Found: C, 76.15; H, 5.12; N, 3.95. CI MS calcd for $C_{21}H_{17}NO_3$ 331.37, found ($M + NH_4^+$) 349.

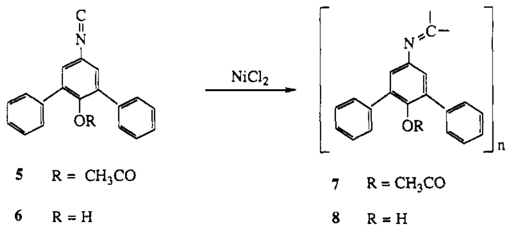
4-Acetoxy-3,5-diphenylphenyl Isocyanide (5). In a three-neck, round-bottomed flask (250 cm^3) equipped with a magnetic bar, a dry ice–acetone condenser, an addition funnel, and a low-temperature thermometer are dissolved the formamide **4** (2.07 g, 6.27 mmol) and dry *N*-methylmorpholine (2.7 cm^3, 3.83 mmol) in 125 cm^3 of dichloromethane. The solution is protected with a blanket of dry N_2 and then cooled to −10 to −3 °C in a dry ice–acetone bath. A solution of diphosgene (0.75 cm^3, 3.135 mmol) in 50 cm^3 of dichloromethane is added through the addition funnel with stirring. The addition took 45 min, with the reaction mixture temperature at −10 to −5 °C, and the dry ice condenser at a temperature below −30 °C. The reaction vessel is warmed to room temperature, and stirring is continued for 2 h. The solution is cooled to 0 °C, and an aqueous solution of Na_2CO_3 (5%, 100 cm^3) is added with stirring maintaining the temperature below 10 °C. Stirring is continued for 15 min at room temperature. The organic phase is separated, washed twice with 50 cm^3 of water, and dried over a 3A molecular sieve. The solvent is rotaevaporated to yield a solid material, which is purified by flash chromatography through a silica gel column under N_2 atmosphere with hexane–chloroform (3/7) as the eluent. The different fractions of the pure material are collected; the solvent is rotaevaporated to leave a solid, which is further dried in a desiccator in the presence of P_2O_5 under full vacuum; yield 1.27 g (65%), mp 84–85 °C, decomposition at higher temperature. Isocyanide **5** has been synthesized in a yield of 62.9% under the same conditions but by using triphosgene. ^{1}H NMR ($CDCl_3$) δ 1.80 (s, 3 H, $COCH_3$), 7.43 (s, 2 H), 7.44 (s, 10 H, phenyl); ^{13}C NMR ($CDCl_3$) δ 20.34 (CH_3), 124.57 (arom C attached to N), 127.55 (C ortho to N=C), 128.29 (C^4 of Ph), 128.50 (C^2 and C^6 of Ph), 128.69 (C^3 and C^5 of Ph), 135.85 (C meta to N=C), 137.55 (C^1 of Ph), 145.54 (C para to N=C), 164.77 (N=C), 168.34 (C=O); IR (neat) 3040, 3020 (m, CH), 2115 (s, NC), 1760 (b, CO), 1590, 1570 (m, C=C) cm^{-1}. Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.82; N, 4.47. Found: C, 80.34; H, 4.79; N, 4.49. EI and CI MS M calcd for $C_{21}H_{15}NO_2$ 313.36, found (M^+) 313, ($M + NH_4^+$) 331.

4-Hydroxy-3,5-diphenylphenyl Isocyanide (6). At ambient temperature, a solution of isocyanide **5** (0.643 g, 1.49 mmol) in 60 cm^3 of methanol is stirred under a N_2 atmosphere in a 100-cm^3 round-bottomed flask. Through an addition funnel an aqueous solution (10 cm^3) of NaOH (0.204 g, 5.1 mmol) is added dropwise. Stirring is continued overnight; then an aqueous solution (200 cm^3) of NH_4Cl (0.278 g, 5.2 mmol) is added to the green solution to give a precipitate, which is filtered and washed many times with water. The white solid is dried in a desiccator in the presence of P_2O_5 under full vacuum (yield 0.40 g (99%), mp 137–138 °C) to give a dark material. ^{1}H NMR ($CDCl_3$) δ 5.7 (s, 1 H, OH), 7.26 (s, 2 H, ortho to NC), 7.47 (s, 10 H, phenyl); ^{13}C NMR ($CDCl_3$) δ 119.61 (arom C attached to N), 127.57 (C ortho to N=C), 128.52 (C^4 of Ph), 129.13 (C^2, C^3, C^5, C^6 of Ph), 129.82 (C meta to N=C), 135.53 (C^1 of Ph), 150.04 (C para to N=C), 162.87 (N=C); IR (KBr) 3340 (br, OH), 2125 (s, NC), 1570, 1585 (w, C=C) cm^{-1}. EI and CI MS M calcd for $C_{19}H_{13}NO$ 271.32, found (M^+) 271, ($M + H^+$) 272.

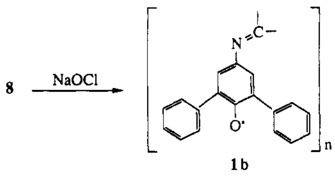
Scheme I



Scheme II



Scheme III



Bis(4-isocyano-2,6-diphenylphenyl) carbonate (3a). ^{1}H NMR ($CDCl_3$) δ 7.3 (s, 10 H, phenyl), 7.5 (s, 2 H, CH ortho to NC); IR (KBr) 3035, 3020 (w, CH), 2118 (s, NC), 1780 (s, CO), 1590, 1570 (m, C=C) cm^{-1}.

Polymerization. General Procedure. In one arm of a Y-shaped polymerization tube is placed a solution of the isocyanide in dichloromethane, and in the other $NiCl_2$ and a magnetic bar. The solution is cooled to −76 °C, and full vacuum is applied. The tube is filled with N_2 and then warmed to room temperature. The process is repeated three times. At ambient temperature the solution of isocyanide is added to $NiCl_2$ with stirring. The reaction is run under a N_2 atmosphere. The solution is then dropped into 100 cm^3 of ether while stirring. The polymer is filtered and washed first with ether, subsequently with small portions of a methanol–water mixture (1:1), and finally ether. It is dried overnight in an oven at 40–60 °C in the presence of P_2O_5 under full vacuum (see Table I).

Poly[(4-acetoxy-3,5-diphenylphenyl)iminomethylene] (7). ^{1}H NMR ($CDCl_3$) δ 1.1–2 (br, 3 H, CH_3), 5.68–7.7 (b, 12 H, arom); ^{13}C NMR ($CH_3OCH_2CH_2OCH_3$) δ 29.1 (CH_3), 119.36 (C ortho to N=C), 126.75 and 127.08 (C^4 of Ph), 127.52 and 127.57 (C^2 and C^6 of Ph), 128.53 and 129.09 (C^3 and C^5 of Ph), 132.83 (C meta to N=C), 135.94 (C para to N=C), 137.59 (C^1 of Ph), 138.15 (arom C attached to N=C), 160.40 (N=C), 167.51 (C=O); IR (KBr) 3020 (m, CH), 1755 (s, CO), 1635 (m, C=N), 1570, 1558 (m, C=C) cm^{-1}. Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.82; N, 4.47. Found: C, 77.48; H, 5.11; N, 4.25.

Poly[(4-hydroxy-3,5-diphenylphenyl)iminomethylene] (8). ^{1}H NMR ($CDCl_3$) δ 5.6–7.5 (br, 13 H, OH and arom); IR (KBr) 3500 (s, OH), 3020 (w, CH), 1650 (br, C=N), 1595 (w, C=C) cm^{-1}.

Poly[(4-oxyl-3,5-diphenylphenyl)iminomethylene] (1b). A solution of polyphenol 8 (0.100 g, 0.37 mmol) in 100 cm^3 of THF is magnetically stirred in a round-bottomed flask equipped with an addition funnel through which an aqueous solution of NaOCl (10%, 1.5 cm^3, 2.02 mmol) is added dropwise under a N_2 atmosphere. After the addition is completed, the dark mixture is stirred for 3.5 h. The solvent is reduced to a few cm^3; the dark solid is filtered and then washed several times with water. The polymer is dried in a desiccator in the presence of P_2O_5 overnight to give 0.089 g (89%) of a black powder. IR (KBr) 3500 (w, OH), 3040 (w, CH), 1640 (sharp, C=N, C-O•), 1610 (m, C-O•) cm^{-1}.

Results and Discussion

Isocyano monomer 5 was obtained in 65% yield by treatment of formamide 4 with diphosgene (Scheme I). Without the protection of the phenolic hydroxyl group, only the carbonate 3a could be isolated, even after a few days in the presence of a strong base (NaOH) at 20 °C. Hydrolysis of 5 afforded monomer 6.

Polymerization of monomers 5 and 6 to polymers 7 and 8 was initiated by nickel chloride in dichloromethane (Scheme II). The reaction took several days, and the yield was not high (Table I). The low conversion is probably due to steric hindrance by the phenyl substituents and to the presence of a donating group para with respect to the isocyano function.[8] The latter effect could be reduced by addition of a Lewis acid, zinc chloride, to monomer 5.

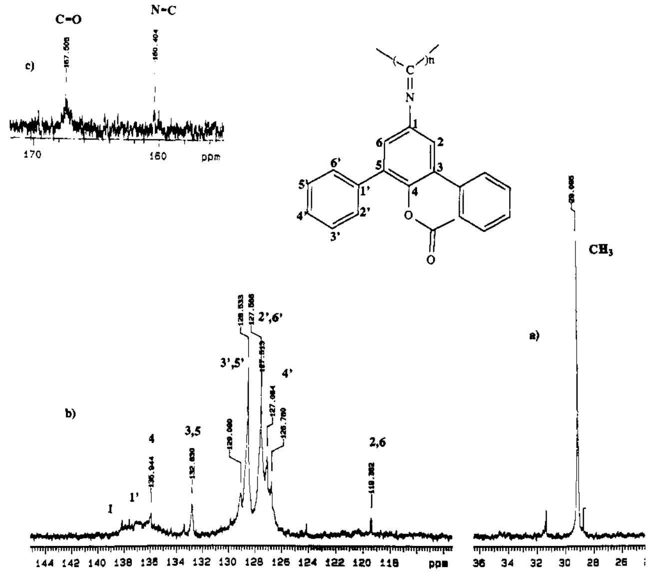


Figure 2. ^{13}C NMR spectrum of polymer 7 with ^{1}H broadband decoupling in ethylene glycol dimethyl ether at 75 °C. The polymer is partly soluble. (a) Expanded part of the aliphatic region. (b) Expanded part of the aromatic region. (c) Expanded part of C=O and N=C regions.

When polyacetate 7 was treated with excess NaOH in a 1:1 methanol/tetrahydrofuran mixture at room temperature, only 20% of the acetate was hydrolyzed to phenolic OH. Therefore, product 8, from the polymerization of 6, was used for the final oxidation affording polyphenoxyl radical 1b (Scheme III), which is a black solid, insoluble in the usual solvents. Sodium hypochlorite is the oxidant of choice; metal oxides and other oxidants were avoided because of the difficulty of their removal from the polymer.

From the viscosity and molecular weight data of the two samples of polymer 7 (from monomer 5, Table I) the constants K and a in the Mark–Houwink–Sakurada equation, $[\eta] = KM^a$, were calculated to be 10^{-7} and 1.3, respectively. This result strongly supports the rigid-rod character of the polymers. Additional support is afforded by the ^{1}H NMR spectra, which are, even at long acquisition times, similar (with very broad peaks) at 400 and 60 MHz.

Table I. Polymerization of Isocyanide[a]

	[monomer], mol/dm^3	[initiator], mol/dm^3	time, h	yield, %	[η], g/dL	M_w[d]	DP$_{exp}$[e]
5	0.227	0.0032[b]	166	29	0.227	52 500	167
5[c]	0.137	0.003	48	64	0.137	35 400	113
6	0.257	0.008	65	43			

[a] See Experimental Section for reaction conditions. [b] Initial concentrations. After 137 h of reaction time more initiator is added; final concentration 0.0096 mol/dm^3. [c] Reaction run in the presence of an equivalent amount of $ZnCl_2$. $ZnCl_2$ is mixed first with the initiator. At the beginning the reaction is heterogeneous; after 5 min it becomes all solid. Dichloromethane (10 cm^3) is then added; 1 h later the reaction mixture is homogeneous. [d] M_w is determined by SEC using polystyrene and poly(methyl methacrylate) standards. [e] Degree of polymerization calculated as the ratio of M_w/(weight of repeating unit).

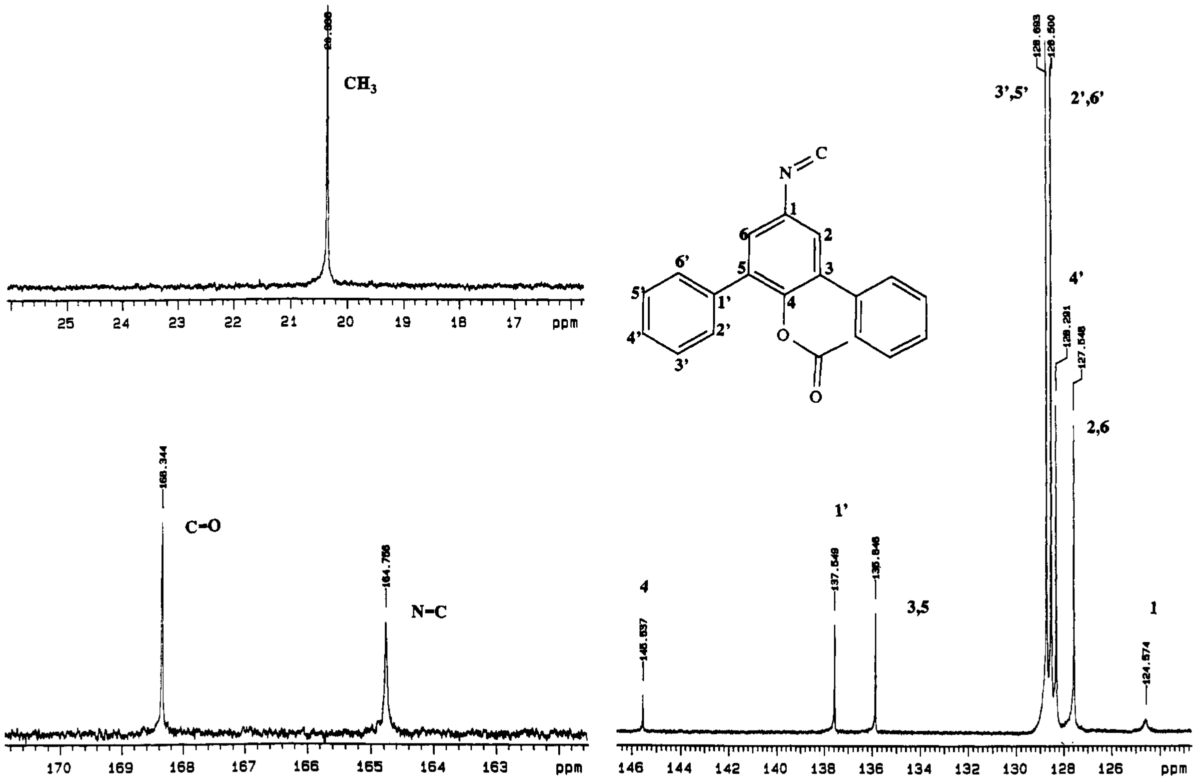


Figure 3. ^{13}C NMR spectrum of monomer 5 in $CDCl_3$ at ambient temperature.

The ^{13}C NMR spectrum of polymer 7 in ethylene glycol dimethyl ether (Figure 2) shows only one peak for the CH_3 carbon. This implies that only one conformer is present, syn and anti isomerism probably not being present. This CH_3 peak has shifted to lower field by 8.76 ppm compared to the monomer (Figure 3), and the C=O carbon peak has shifted to higher field by 0.94 ppm. Both shifts will be due to ring current effects or steric compression or both.

Powder ESR spectra of a sample of polymer **1b** showed a single broad resonance at a *g* value of 2.0044. The peak-to-peak line width amounted to 7 G at ambient temperature and it increased to only 9 G at 4 K, while the intensity of the resonance increased by a factor of 2 in this temperature region. These results suggest the absence of any short-range ordering among the unpaired spins of polymer **1b**. Further evidence for the absence of ordering is found in magnetic susceptibility (χ_m) measurements, as performed in the temperature region 77–320 K. A plot of χ_m versus $1/T$ shows the presence of a high diamagnetic (χ_d) contribution. A linear relation was found between $1/(\chi_m - \chi_d)$ and temperature (Figure 4). The plot is again illustrative of a paramagnet without short-range ordering among unpaired spins in the temperature region studied. From the slope of this plot we calculated a spin density of 1.8×10^{21} spins/g, assuming a density of the polymer of 1 g/cm^3. This spin density is equivalent to approximately 0.8 spin/repeating unit, which is high in view of the synthetic route including the final oxidation.

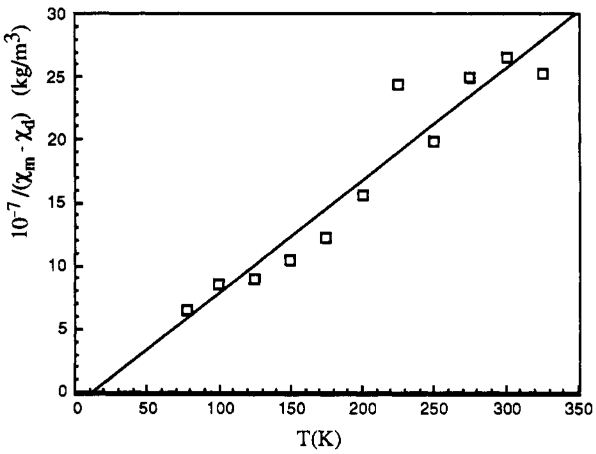


Figure 4. Reciprocal of $\chi_m - \chi_d$ as a function of temperature.

The thermal stability of this polymer has been monitored at ambient temperature and at −30 °C by observation of the C–O$^\bullet$ stretching frequencies at 1640 (partly obscured by C=N) and 1610 cm^{-1} in the infrared absorption spectrum. The polymer was found to be stable for months at ambient temperature when present in a KBr pellet.

In this paper a route is described to a polymer with a high concentration of free radicals. Evidence is presented of a stacking and close packing of these free radicals in rigid-rod polymer molecules. Long-range spin-spin interactions have, however, not been observed. Arguments to explain the absence of such coupling could be as follows:

There is the loss of approximately 20% of free radicals during synthesis, which could be detrimental for the magnetic properties.

According to McConnell's theory a negative value of the product of spin densities at two neighboring sites would predict ferromagnetism and a positive value antiferromagnetism (see refs 21 and 22). An exactly perpendicular stacking would lead to a positive sign. Possibly, the stacking is not exactly perpendicular and the product of spin densities is vanishingly small.

Acknowledgment. We acknowledge the experimental support by H. W. van Kesteren and G. J. M. Poodt at Philips Research Laboratories, Eindhoven, and the recording of almost all NMR spectra by Dr. A. M. Kenwright, Department of Chemistry, University of Durham, UK.

Registry No. **2**, 50432-01-4; **3**, 134334-14-8; **3a**, 134334-18-2; **4**, 134334-15-9; **5**, 134334-16-0; **5** (homopolymer), 134334-20-6; **6**, 134334-17-1; **6** (homopolymer), 134334-21-7; **7** (SRU), 134334-23-9; **8** (SRU), 134334-24-0; HCO_2H, 64-18-6; CH_3COCl, 75-36-5.

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Aging Processes of Alumina Sol-Gels: Characterization of New Aluminum Polyoxycations by ^{27}Al NMR Spectroscopy

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The existence of unidentified molecular aluminum oxide clusters has been previously postulated in many alumina sols produced by various methods. We have used ^{27}Al NMR spectroscopy kinetic studies to identify three new polyoxyaluminum cations in these sols, which we show are formed by thermal transformation of the well-known tridecamer cation $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$. These clusters, which we denote as AlP_1, AlP_2, and AlP_3, have resonances at 64.5 ppm (tetrahedral Al site)/$\approx$10 ppm (octahedral Al site), 70.2 ppm (tet)/10.0 ppm (oct), and 75.6 ppm (tet)/9.3 ppm (oct), respectively. NMR and gel permeation chromatography data suggest that the poly(oxyaluminum) cation AlP_2, which dominates this reaction process, is a dimer of Al_{13}. A mechanism for the aging process is proposed.

Introduction

Alumina sol-gels are complex, multicomponent fluids that are precursors for many materials such as controlled-porosity ceramic membranes, refractory fibers, coatings,[1] and optical matrices.[2] They are commonly formed from the hydrolysis of aluminum alkoxides, but they can also be produced by the polymerization of hydrated aluminum cations. The chemistry of these systems is still poorly defined, despite many years of study. We do know, however, that the nature of the elementary alumina species defines the bonding and microstructure in the sol. Given the importance of alumina sol-gel chemistry, this has motivated our studies to gain a fundamental understanding of the processes that control chemical composition and microstructure.

Past studies in this laboratory have centered on the alkoxide hydrolysis process. We have recently determined that the hydrolysis of aluminum alkoxides at high H_2O/Al ratios at elevated temperature leads to the formation of small colloidal particles of aluminum hydroxyoxide linked together to form an open, tenuous fractal structure.[3] The acid/Al ratio determines the degree of compactness of the network. Our small-angle neutron scattering experiments have revealed that the subunits of this fractal network are about 10-25 Å in diameter. Previous work has also shown that at room temperature, hydrolysis at high acid/Al ratios leads to the formation of alumina sols in which the $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ cation accounts for about 70% of the aluminum present.[4,5] We observed that aging these sols at 90 °C produced an unidentified species before gelation of the sol occurred. This molecule had a characteristic ^{27}Al NMR resonance at 70 ppm to high frequency (downfield) from $Al(H_2O)_6^{3+}$. In an effort to characterize this species and to better understand the steps in the aging and gelation process, we turned to the hydrolysis of aluminum salts in solution as a method of forming more characterizable sols.

At low pH (<3), aluminum salts exist in aqueous solutions as the hydrated Al^{3+} cation. An increase in pH leads to the removal of H^+ from the coordinated water mole-

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