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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 NiCl2-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 and by Yamamoto and other Japanese workers. A large variety of isocyanides have been polymerized by our group, applying nickel(II) salts as catalysts. Poly(iminomethylene)s or poly(carbonimidoyls), are rigid rods with a helical configuration; there are approximately four R—N=C< units per helical turn. 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. 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.

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. 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. A polymer of (3,5-di-tert-butyl-4-hydroxyphenyl)acetylene has been synthesized by Tsuchida et al. 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 polyladdicals, 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 300A and a VXR 400S instruments at 60 and 400 MHz for 1H and on a Varian VXR 400S instrument at 100 MHz for 13C; the chemical shifts are reported in ppm downfield from TMS for 1H and 13C. The 13C 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 Pigel 10a. A Roth Scientific Ltd. Visctec 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 FF5 and FP51.
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 V 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 cm³ 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 cm³) with stirring. Toluene (dry, 160 cm³) is added; the mixture is protected with a blanket of N₂, 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 cm³. 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 hydroxide carbonate and water, and finally toluene. It is dried in a desiccator in the presence of phosphorus pentoxide under full vacuum; yield 11.5 g (85%), mp 167–168 °C. *H NMR (CDCl₃, 6.27 ppm) shows the signals of aromatic protons and formamide (4.07 ppm) is assigned to the proton on the amine group (98% purity).

4-Acetoxy-3,5-diphenylphenyl Isocyanide (4). A mixture of formamide (3.1.44 g, 5.02 mmol), triethylamine (0.7 cm³, 5.05 mmol) and dichloromethane (dry, 100 cm³) is placed in a round-bottomed flask (250 cm³) equipped with an addition funnel and a guard tube of CaCl₂. The heterogeneous mixture is cooled with an ice bath, and a solution of acetyl chloride (0.36 cm³, 5.67 mmol) in 5 cm³ 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 cm³ of water, then dried over 4 A molecular sieves. The solvent is rotary evaporated to leave a solid, which is dried again in a desiccator in the presence of P₂O₅ under vacuum; yield 1.342 g (81%), mp 72–75 °C. *H NMR (CDCl₃, 400 MHz), two isomers, δ 1.782 and 1.784 (s, 3 H, CH₃), 7.08 and 7.53 (s, 2 H, arorn ortho to N–C=O), 7.36–7.42 (m, 10 H, Ph.), 8.02 and 8.69 (br, 1 H, NH), 5.2 and 5.67 (d, 1 H, NH, H–C=O); *¹C NMR (CDCl₃), two isomers (the first cited shift corresponds to the predominant isomer, the second one to the minor isomer) δ 20.45 and 20.34 (CH₃), 121.35 and 120.11 (C ortho to N–C=O), 127.67 and 127.94 (C of Ph), 128.25 and 128.37 (C of Ph), 128.78 and 128.69 (C 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 of Ph), 140.30 and 142.22 (C para to N–C=O), 159.29 and 162.66 (N–C=O–C), 168.46 and 168.18 (O–C=O–C). IR (KBr) 3280 (br, NH), 3040 (m, CH), 1752 (s, CO-CH₃), 1680 and 1653 (s, CO-NH), 1585 (m, Ph), 1565 (w, Ph cm⁻¹). Anal. Caled. for C₁₇H₁₃NO₂: C, 82.87, H, 4.79; Found: C, 82.86, H, 4.82. EI and CI MS: m/z 176.06 (M⁺), m/z 293.15 (M⁺ + H⁺) 131.
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 NiCl₂ and a magnetic bar. The solution is cooled to -78 °C, and full vacuum is applied. The tube is filled with N₂ and then warmed to room temperature. The process is repeated three times. At ambient temperature the solution of isocyanide is added to NiCl₂ with stirring. The reaction is run under a N₂ atmosphere. The solution is then dropped into a nol-water mixture 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 P₂O₅ under full vacuum (see Table I).

Poly[(4-acetoxy-3,5-diphenylphenyl)iminomethylen] (7).

\[ \text{Polymerization of monomers 5 and 6 to polymers 7 and 8 was initiated by nickel chloride in dichloromethane} \]

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

Results and Discussion

Isocyanato 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 I

Bis(4-isocyano-2,6-diphenylphenyl) carbonate (3a). \[\text{In one arm of a Y-shaped polymerization tube is placed a solution of the isocyanide in dichloromethane, and in the other NiCl₂ and a magnetic bar. The solution is cooled to } -78 \degree \text{C, and full vacuum is applied. The tube is filled with } N₂ \text{ and then warmed to room temperature. The process is repeated three times. At ambient temperature the solution of isocyanide is added to NiCl₂ with stirring. The reaction is run under a } N₂ \text{ atmosphere. The solution is then dropped into a nol-water mixture first with ether, subsequently with small portions of a methanol-water mixture (1:1), and finally ether. It is dried overnight in an oven at } 40-60 \degree \text{C in the presence of } P₂O₅ \text{ under full vacuum (see Table I).} \]

Poly[(4-hydroxy-3,5-diphenylphenyl)iminomethylene] (8).

Polymerization of monomers 5 and 6 to polymers 7 and 8 was initiated by nickel chloride in dichloromethane

Scheme II

Scheme III

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

(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 isocyanato function.\[\text{The latter effect could be reduced by addition of a Lewis acid, zinc chloride, to monomer 5.}\]

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, \[\text{[7]} = KM^n,\] 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\text{H} \text{NMR spectra, which are, even at long acquisition times, similar (with very broad peaks) at } 400 \text{ and } 60 \text{ MHz.} \]
Table I. Polymerization of Isocyanide

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<th>[monomer], mol/dm³</th>
<th>[initiator], mol/dm³</th>
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<th>yield, %</th>
<th>[η], g/dL</th>
<th>$M_w$, d</th>
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<td>0.008</td>
<td>65</td>
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</table>

See Experimental Section for reaction conditions. Initial concentrations. After 137 h of reaction time more initiator is added; final concentration 0.0096 mol/dm³. Reaction run in the presence of an equivalent amount of ZnCl₂. ZnCl₂ is mixed first with the initiator. At the beginning the reaction is heterogeneous; after 5 min it becomes all solid. Dichloromethane (10 cm³) is then added; 1 h later the reaction mixture is homogeneous. $M_w$ is determined by SEC using polystyrene and poly(methyl methacrylate) standards. *Degree of polymerization calculated as the ratio of $M_w$/ (weight of repeating unit).

Figure 3. $^{13}$C NMR spectrum of monomer 5 in CDCl₃ at ambient temperature.

The $^{13}$C NMR spectrum of polymer 7 in ethylene glycol dimethyl ether (Figure 2) shows only one peak for the CH₃ carbon. This implies that only one conformer is present, syn and anti isomerism probably not being present. This CH₃ 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 ($x_m$) measurements, as performed in the temperature region 77–320 K. A plot of $x_m$ versus $1/T$ shows the presence of a high diamagnetic ($x_d$) contribution. A linear relation was found between $1/(x_m - x_d)$ 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 $1.8 \times 10^{21}$ spins/g, assuming a density of the polymer of 1 g/cm³. 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.

The thermal stability of this polymer has been monitored at ambient temperature and at −30 °C by observation of the C=O° 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.

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Registry No. 2, 50432-01-4; 3, 134334-14-8; 3a, 134334-18-2; 4, 13434-15-9; 5, 13434-16-0; 6 (homopolymer), 13434-20-6; 6, 13434-17-1; 7 (SRU), 13434-23-9; 8 (SRU), 13434-24-0; HCO3H, 64-18-6; CH3COCl, 75-36-5.

Aging Processes of Alumina Sol–Gels: Characterization of New Aluminum Polyoxycations by 27Al 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 27Al NMR spectroscopy kinetic studies to identify three new polyoxyaluminate cations in these sols, which we show are formed by thermal transformation of the well-known tridecamer cation Alα3O(1/2)(OH)11(H2O)112+. These clusters, which we denote as AIP, AIP2, and AIP3, have resonances at 64.5 ppm (tetravalent Al site)/≈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 AIP2, which dominates this reaction process, is a dimer of Al13.

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 H2O/Al ratios at elevated temperature leads to the formation of small colloidal particles of aluminum hydroxide 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 Alα3O(1/2)(OH)11(H2O)112+ cation accounts for about 70% of the aluminum present.4 We observed that aging these sols at 90 °C produced an unidentified species before gelation of the sol occurred. This molecule had a characteristic 27Al NMR resonance at 70 ppm to high frequency (downfield) from Al(H2O)63+. 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 Al3+ cation. An increase in pH leads to the removal of H+ from the coordinated water mole-