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Abdelkader, M.; Drenth, W.; Meijer, E.W.

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

M. Abdelkader and W. Drenth

Department of Organic Chemistry, University at Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

E. W. Meijer

Philips Research Laboratories, PO Box 80.000, 5600 JA Eindhoven, The Netherlands

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Polymer 1b, [R—N=C<], 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 Millich4 and by Yamamoto and other Japanese workers.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(aminomethylene) or poly(carboximidoxy), 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(aminomethylene) 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 pendant radical, 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 Tsuda 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 nitroxy! 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 13C; the chemical shifts are reported in ppm downfield from TMS for 1H and 13C. The 1H 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. Viscolec 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 FF51

References

A Stable Poly(aminomethylene) use and dried if noted. Microanalysis Group, Department of Chemistry, University of Cambridge, performed by the Elemental Analytical Section of the Institute for Applied Chemistry. The Netherlands, and by the Microanalysis Group, Department of Chemistry, University of Durham, Durham, UK. EI and CI MS are performed on a 7070 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-aminoo-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 formamidine crystallizes at room temperature (powder). It is filtered and washed first with small portions of toluene, followed by water, a solution of sodium hydroxide and water, and finally toluene. It is dried in a desiccator in the presence of phosphorous pentoxide under full vacuum; yield 11.5 g (85%), mp 167–168 °C. 'H NMR (CDCl₃, 60 MHz) δ 7.55 (s, 2 H, CH ortho to N-C=O), 7.2–7.65 (m, 10 H, phenyl), 8.2 (m, 1 H, CH para to N-C=O), 9.62 (b, 1 H, NH); ¹³C NMR (DMSO-d₆) δ 133.68 (C₃ and C₅ of Ph), 129.46 and 129.55 (C¹ and C⁷ of Ph), 131.52 and 132.22 (C meta to N-C=O), 131.59 and 131.46 (arom CH attached to N), 138.72 and 138.49 (C⁴ of Ph), 146.69 and 144.16 (C para to N-C=O), 159.46 and 162.98 (C=O); IR (KBr) 2890 (w, NH₄⁺), 3313.37 (v, NH₄⁺), 1691.46 and 1691.18 (C=O); IR (KBr) 3280 (br, NH, 3040 (m, CH), 1752 (s, CO-CH₃), 1680 and 1535 (s, CO-NH), 1585 (w, C=O); IR 1540 (s, CO-CH₃), 1291.35 (s, CO-CH₃), 1150 (s, CO-CH₃), 1020 (s, CO-CH₃). Anal. Calcd for C₂₈H₂₁NO₃: C, 84.35; H, 5.05; N, 4.49. Found: C, 84.62; H, 5.12; N, 4.47. EI and CI MS calcd for C₂₈H₂₁NO₃ 313.36, found (M + NH₄⁺) 313, (M + NH₄⁺) 331.

4-Acetoxy-3,5-diphenylphenyl Isocyanide (5). In a three-neck, round-bottomed flask (250 cm³) equipped with a magnetic bar, a dry ice-acetone condenser, an addition funnel, and a low-temperature thermometer are dissolved formamide (0.75 cm³, 10 mmol) and dichloromethane (dry, 129 cm³) with stirring. The addition took 30 min. Then, acetyl chloride (0.278 g, 0.643 g, 1.49 mmol) is added with stirring maintaining the temperature below 0 °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 Na₂CO₃ (5%, 100 cm³) 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 cm³ of water, and dried over a 3 Å molecular sieve. The solvent is rotocastor to yield a solid material, which is purified by flash chromatography through a silica gel column under N₂ atmosphere with hexane-chloroform (3/7) as the eluent. The different fractions of the pure material are collected; the solvent is rotocastor to leave a solid, which is further dried in a desiccator in the presence of P₂O₅ 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 without isocyanide triphenylamine. 'H NMR (CDCl₃, 300 MHz) δ 1.80 (s, 3 H, COCH₃), 7.34 (s, 2 H), 7.44 (s, 10 H, phenyl); ¹³C NMR (CDCl₃) δ 20.34 (CH₃), 124.57 (arom CH attached to N), 127.55 (C ortho to N=C), 128.29 (C para to N=C), 128.50 (C¹ and C⁷ of Ph), 128.69 (C³ and C⁵ of Ph), 135.85 (C meta to N=C), 135.75 (C² of Ph), 145.54 (C para to N=C, 164.77 (N=C), 168.34 (CO-CH₃); IR (neat) 3040, 3020 (m, CH), 2115 (s, NC), 1780 (b, CO), 1590, 1570 (C=O cm⁻¹). Anal. Calcd for C₂₇H₂₂N₂O₃: C, 86.44; H, 4.47; N, 4.47. Found: C, 86.54; H, 4.79; N, 4.49. EI and CI MS calcd for C₂₇H₂₂N₂O₃ 313.36, found (M⁺) 313, (M + NH₄⁺) 331.

4-Hydroxy-3,5-diphenylphenyl Isocyanide (6). At ambient temperature, a solution of isocyanide 5 (0.643 g, 1.49 mmol) in 60 cm³ of methanol is stirred under a N₂ atmosphere in a 100-cm³ round-bottomed flask. Through an addition funnel an aqueous solution (10 cm³ of NaOH (0.204 g, 5.1 mmol) is added dropwise. Stirring is continued overnight; then an aqueous solution of NH₄Cl (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 solid is dried in a desiccator in the presence of P₂O₅ under full vacuum (yield 0.40 g (99%)), mp 137–138 °C to give a dark material. 'H NMR (CDCl₃) δ 7.5 (s, 1 H, OCH₃), 7.26 (s, 2 H, ortho to NO), 7.47 (s, 10 H, phenyl); ¹³C NMR (CDCl₃) δ 119.16 (arom CH attached to N), 129.13 (C¹, C³, C⁵ of Ph), 129.82 (C meta to N=C), 135.83 (C² of Ph), 150.04 (C para to N=C), 162.87 (N=C=O); IR (KBr) 3400 (br, OH), 2125 (w, NH), 1570, 1565 (w, C=O cm⁻¹). EI and CI MS calcd for C₂₉H₂₄N₂O₄ 313.38, found (M⁺) 313, (M + NH₄⁺) 331.
Bis(4-isocynano-2,6-diphenylphenyl) carbonate (3a). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 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 isocynane in dichloromethane, and in the other NiCl\(_2\) and a magnetic bar. The solution is cooled to \(-78^\circ\)C, and full vacuum is applied. The tube is filled with \(\text{N}_2\) 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 in dichloromethane, and in the other NiCl\(_2\) and a magnetic bar. The solution is cooled to 3.5 to water mixture. After the addition is completed, the dark mixture is stirred for 60 min. The solvent is reduced to a few cm\(^3\); the dark solid is magnetically stirred in a round-bottomed flask equipped with an addition funnel through which an aqueous solution of NaOCl is added dropwise under a \(\text{N}_2\) 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 \(^\circ\)C in the presence of \(\text{P}_2\text{O}_5\) under full vacuum (see Table I).

**Poly[(4-acetoxy-3,5-diphenylphenyl)iminomethylene] (7).** \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.1-2.0 (br, 3 H, CH\(_3\)), 5.6-7.5 (l:1), 1.1-2 (br, CH\(_2\)), 5.68-7.7 (s, 10 H, CH\(_3\)), 5.11; 5.68-7.7 (s, 10 H, CH\(_3\)), 5.68-7.7 (s, 10 H, CH\(_3\)), 5.11; 5.68-7.7 (s, 10 H, CH\(_3\)), 5.11; 5.68-7.7 (s, 10 H, CH\(_3\)), 5.11; 5.68-7.7 (s, 10 H, CH\(_3\)), 5.11; 5.68-7.7 (s, 10 H, CH\(_3\)), 5.11; 5.68-7.7 (s, 10 H, CH\(_3\)), 5.11; 5.68-7.7 (s, 10 H, CH\(_3\)), 5.11; 5.68-7.7 (s, 10 H, CH\(_3\)), 5.11; 5.68-7.7 (s, 10 H, CH\(_3\)), 5.11; 5.68-7.7 (s, 10 H, CH\(_3\)), 5.11; 5.68-7.7 (s, 10 H, CH\(_3\)), 5.11; 5.68-7.7 (s, 10 H, CH\(_3\)), 5.11; 5.68-7.7 (s, 10 H, CH\(_3\)), 5.11. Anal. Calcd for C\(_{32}\)H\(_{28}\)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\(_3\)) \(\delta\) 5.6-7.5 (br, 13 H, OH and arom); IR (KBr) 3500 (s, OH), 3020 (w, CH), 1650 (br, C=O), 1586 (w, C=C) cm\(^{-1}\).

**Results and Discussion**

Isocynano 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 \(^\circ\)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 isocyanane function. 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, \(\eta = KM^a\), were calculated to be 10\(^{-2}\) 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 low acquisition times, similar (with very broad peaks) at 400 and 60 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>Mw, a</th>
<th>DP, c</th>
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<td>48</td>
<td>64</td>
<td>0.137</td>
<td>35400</td>
<td>113</td>
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<tr>
<td>6</td>
<td>0.257</td>
<td>65</td>
<td>43</td>
<td></td>
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</table>

*See Experimental Section for reaction conditions. a Initial concentrations. After 137 h of reaction time more initiator is added; final concentration 0.0096 mol/dm³. b 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. c Mw is determined by SEC using polystyrene and poly(methyl methacrylate) standards. d Degree of polymerization calculated as the ratio of Mw/(weight of repeating unit).

Figure 3. 13C NMR spectrum of monomer 5 in CDCl₃ at ambient temperature.

The 13C 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 (χm) measurements, as performed in the temperature region 77–320 K. A plot of χm versus 1/T shows the presence of a high diamagnetic (χd) contribution. A linear relation was found between 1/(χm – χd) 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 × 10⁻²⁶ 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

Figure 4. Reciprocal of χm – χd as a function of temperature.
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, 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\textsubscript{2}H, 64-18-6; CH\textsubscript{3}COCl, 75-36-5.

Aging Processes of Alumina Sol–Gels: Characterization of New Aluminum Polyoxyocations by \textsuperscript{27}Al NMR Spectroscopy

G. Fu and L. F. Nazar\textsuperscript{*}

Department of Chemistry, University of Waterloo, Guelph-Waterloo Centre for Graduate Work in Chemistry, Waterloo, Ontario, Canada N2L 3G1

A. D. Bain

Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1

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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 \textsuperscript{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\textsubscript{13}O\textsubscript{4}(OH)\textsubscript{24}(H\textsubscript{2}O)\textsubscript{12}\textsuperscript{3+}. These clusters, which we denote as AlP\textsubscript{1}, AlP\textsubscript{2}, and AlP\textsubscript{3}, have resonances at 64.5 ppm (tetrahedral 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 AlP\textsubscript{2}, which dominates this reaction process, is a dimer of Al\textsubscript{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, and optical matrices.\textsuperscript{3} 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\textsubscript{2}O/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.\textsuperscript{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 by high acid/Al ratios leads to the formation of alumina sols in which the Al\textsubscript{13}O\textsubscript{4}(OH)\textsubscript{24}(H\textsubscript{2}O)\textsubscript{12}\textsuperscript{3+} cation accounts for about 70% of the aluminum present.\textsuperscript{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 \textsuperscript{27}Al NMR resonance at 70 ppm to high frequency (downfield) from Al(H\textsubscript{2}O)\textsubscript{6}\textsuperscript{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\textsuperscript{3+} cation. An increase in pH leads to the removal of H\textsuperscript{+} from the coordinated water mol-