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

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Polymers of isocyanides, more systematically called poly(aminomethylenes) 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(aminomethylenes) 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 pendant 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 Tsuda et al. and oxidized to the corresponding phenoxy 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 phenoxy radicals. These phenoxy 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 phenoxy 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 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. ViscoTech 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.

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.

Polymers of isocyanides, more systematically called poly(aminomethylenes) 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(aminomethylenes) 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.

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A Stable Poly(iminomethylene)

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 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 from light and the vessel is placed in an oil bath. Stirring is continued, and the bath temperature is raised to 150 °C. Isocyanide is added, and 110–120 °C is reached. The reaction mixture is stirred for 15 min, with the reaction mixture at –10 to –5 °C, and the cold ice-acetate bath is added. After stirring for 15 min at 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 continues 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 distilled through a small solid, 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 solid is recrystallized from 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 50 cm³ of water, then dried over 4 Å molecular sieve. The solution is distilled to 0.40 g (99%), mp 137–138 °C to give a dark material.

4-Hydroxy-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, formic acid (107 g, 2.67 mmol) and dry N-methylmorpholine (5.05 cm³, 8.33 mmol) in 125 cm³ of dichloromethane. The solution is protected with a blanket of dry N₂ and then cooled to –10 to –5 °C in a dry ice-acetone bath. A solution of diphosgene (0.75 cm³, 3.15 mmol) is added in 50 cm³ 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 cold ice-acetate bath 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 Na₂CO₃ (5%, 100 cm³) is added with stirring maintaining the temperature below 10 °C. Stirring continues 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 distilled through a small solid, 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 solid is recrystallized from the addition funnel dropwise with magnetic stirring over 20 min.

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Bis(4-isocyno-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 isocyanide in dichloromethane, and in the other NiCl\(_2\) and a magnetic bar. The solution is cooled to \(-78^\circ\text{C}\), 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 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 \(^\circ\text{C}\) in the presence of P\(_2\)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 (br, 3 H, CH\(_3\)), 5.6-7.5 (13 H), 135.94 (C\(_{1}\) of Ph), 163.5 (C=O); IR (KBr) 3020 (w, CH), 1595 (s, CO); \(\delta\) 29.1 (C meta to N=C), 128.53 and 129.09 (C\(_{1}\) and C\(_{6}\) of Ph), 132.83 (C meta to N=C), 135.94 (C para to N=C), 157.59 (C=O of Ph), 138.15 (arom C attached to N=C), 167.51 (C=O); IR (KBr) 3020 (m, CH), 1755 (s, CO), 1635 (m, C=O), 1570, 1558 (m, C=O) cm\(^{-1}\). Anal. Calcd for C\(_{56}\)H\(_{46}\)O\(_4\): 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=N), 1595 (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 \(^\circ\text{C}\). Hydrolysis of 5 afforded monomer 6.

Polymerization of monomers 5 and 6 to polymers 7 and 8 was initiated by nickel chloride in dichloromethane due to steric hindrance by the phenyl substituents and to the presence of a donating group para with respect to the isocynano function. \(^6\) 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 \(10^{-7}\) and 1.3, respectively. This result strongly supports the rigid-rod character of the polymers. Additional support is afforded by the \(^1H\) NMR spectra, which are, even at long acquisition times, similar (with very broad peaks) at 400 and 60 MHz.
Table I. Polymerization of Isocyanide

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<th>[initiator], mol/dm³</th>
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<th>yield, %</th>
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*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. dM_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. 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.

Figure 4. Reciprocal of x_m - x_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 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...
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 polyoxyluminum cations in these sols, which we show are formed by thermal transformation of the well-known tridecamer cation $\text{Al}_{13}\text{O}_{4}\text{(OH)}_{24}(\text{H}_{2}\text{O})_{12}^{2+}$. These clusters, which we denote as $\text{AlP}_{1}$, $\text{AlP}_{2}$, and $\text{AlP}_{3}$, have resonances at 64.5 ppm (tetrahedral Al site)/≈10 ppm (octahedral Al site), 70.2 ppm (tet)/9.3 ppm (oct), and 75.6 ppm (tet)/9.3 ppm (oct), respectively. NMR and gel permeation chromatography data suggest that the poly(oxyaluminum) cation $\text{AlP}_{2}$, which dominates this reaction process, is a dimer of $\text{Al}_{13}^{2+}$. 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. 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 alkaline hydrolysis process. We have recently determined that the hydrolysis of aluminum alkoxides at high $\text{H}_{2}\text{O}/\text{Al}$ ratios at elevated temperature leads to the formation of small colloidal particles of aluminum hydroxyoxide linked together to form an open, tenuous fractal structure. 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 $\text{Al}_{13}\text{O}_{4}\text{(OH)}_{24}(\text{H}_{2}\text{O})_{12}^{2+}$ cation accounts for about 70% of the aluminum present. 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 $\text{Al}(\text{H}_{2}\text{O})^{6+}$. 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 characteristic sols.

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

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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; $\text{HCO}_{2}\text{H}$, 64-18-6; $\text{CH}_{3}\text{COCl}$, 75-36-5.

References