in the spectrum of the reaction mixture having reacted overnight (see above), are assigned to the N—CH₃ and the H—C= signals of 9 (R¹ = H), respectively. This was confirmed when after an overnight reaction the ¹H-NMR spectra of the solutions of 1b, 1c and 1d in N₂D₄-D₂O were measured. In the case of 1c and 1d the low field region a peak is observed between δ 7.03-7.09 i.e. the HC= in 9 (R¹ = H) where in the case of 1b this low-field singlet is absent but a peak is observed in the high field region at δ 1.87 i.e. the CH₃ in 9 (R¹ = CH₃). The three pyrazoles 8b, 8c and 8d which were isolated from the analogous reaction of the pyrimidinium salts 1b, 1c and 1d, are all deuterated at position 4. It was observed further that the 3,5-dimethyl-4-D-pyrazole (8c) also contains deuterium in the methyl group as proved by the presence of peaks at m/e = M, M + 1, M + 2, M + 3, M + 4 and M + 5 in the mass spectrum. Apparently, in the open-chain compounds 3, 4 and 5 the methyl group participates in the tautomerism since the alternative possibility — a H/D exchange in the methyl group of 3,5-dimethyl-4-D-pyrazole does not take place under these mild conditions.

**Experimental part**

The ¹H-NMR spectra were recorded on a Jeol JNM-C60 H spectrometer, using TMS (δ = 0) as internal standard. In the case of adducts the apparatus was equipped with a JES-VT-3 variable temperature controller. Measurements of D contents were carried out on an AEI-MS 902 mass spectrometer.

**Preparation of the starting materials**

1-Methylpyrimidinium iodide (1a), 1,2-dimethylpyrimidinium iodide³ (1b), 1,4,6-trimethylpyrimidinium iodide⁴ (1c) and 4-phenyl-1-methylpyrimidinium iodide¹⁴ (1d) were prepared as described in the literature.

**Poly(iminomethylene), 7¹, Synthesis of diphenylphosphine-substituted poly[(1-phenylethyl)iminomethylene]**

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Department of Organic Chemistry of the University, Croesestraat 79, Utrecht, The Netherlands (Received August 31st, 1977)

**Abstract.** Polymer-anchored phosphine functions were obtained in two ways: by diphenylphosphinilation of poly[[1-(4-bromophenylethyl)iminomethylene] and by polymerization of 1-[4(diphenylphosphino)phenyl]-1-isocyanatothene. The synthesis of the monomers and polymers is described.

**Introduction**

Many efforts have been made at anchoring homogeneous catalysts on insoluble supports. For this purpose materials like silica² and polystyrene³,⁴ have frequently been used. This immobilization of a catalyst sometimes diminishes side-reactions⁵ and extends its lifetime. The anchoring of homogeneous catalysts on the usual types of polymeric supports suffers from a number of disadvantages. In most cases the secondary structure of the polymers and the surroundings of the catalytic centres are unknown. Often, the accessibility of the complex is reduced, giving rise to lower activities. The degree of introduction of phosphine groups, often used as interfaces between polymer and metal ion, appears to be low: 1 per 3-20 polymer side chains⁶,⁷. Moreover, the polymers usually contain some

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residual chlorine or bromine. In earlier papers Millich\textsuperscript{4} and wc\textsuperscript{10,11} showed that poly(minimethylene)s have the configuration of a tightly coiled helix with side-chains protruding from a rodlike main chain. This property gives poly(minimethylene)s major advantages for catalyst attachment: the catalytic centres are more accessible and the secondary structure is more uniform and better defined. The chirality of the main chain might be attractive for asymmetric catalysis.

In this paper we describe the synthesis of two types of triphenylphosphine containing poly(minimethylene). The first type was made by diphenylphosphination of poly[(1-(4-bromo-phenyl)ethyl][iminomethylene]. The second type was synthesized by polymerization of a triphenylphosphine containing isocyanide. Applications of these polymers in catalysis will be described in subsequent papers of this series.

Results and discussion

Millich has described the synthesis of 1-phenylethyl isocyanide and its polymerization by means of an acid-coated glass catalyst\textsuperscript{12}. We have synthesized 1-(4-bromophenyl)-ethyl isocyanide, (3), in an analogous way starting from 4-bromoacetophenone (Scheme 1). Polymerization of 3 was accomplished by nickel chloride\textsuperscript{13}. The intrinsic viscosity of the polymer obtained, (4), was 0.31 dl/g. If we use the values of the Mark-Houwink constants determined for poly[1-phenylethyl]iminomethylene]\textsuperscript{14} to estimate the molecular weight, a value of 40,000 is calculated.

The introduction of diphenylphosphine functions into the polymer 4 was realized through lithiation with butyllithium and subsequent coupling with chlorodiphenylphosphine. The effect of the reaction conditions on the degree of exchange of bromine in 4 was determined from the elemental analysis (Table I). The highest degree of functionalization, 50\%, was obtained in 5b. This value is appreciably higher than most of the values reported for polystyrene resins\textsuperscript{4,7,8}. An explanation for this difference could be the better accessibility of the side groups in poly(minimethylene).

Table I Lithiation of polymer 4 and coupling with chlorodiphosphinophosphate.

<table>
<thead>
<tr>
<th>Polymer\textsuperscript{a}</th>
<th>Polymer composition\textsuperscript{b}</th>
<th>% Lithiation</th>
<th>% Coupling</th>
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<tr>
<td>5a</td>
<td>0.62 0.21 0.17</td>
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<tr>
<td>5b</td>
<td>0.40 0.11 0.49</td>
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\textsuperscript{a} Reaction conditions 5a: 1.3 eq. BuLi, reaction time 2 h; 3.2 eq. Ph\textsubscript{2}PCl, reaction time 4 h; 5b: 2.1 eq. BuLi, reaction time 3 h; 7.2 eq. Ph\textsubscript{2}PCl, reaction time 96 h.

\textsuperscript{b} m, n and o are the fractions of unsubstituted, bromine substituted and phosphine substituted phenyl groups, respectively.

Just like functionalized polystyrene resins, polymer 5 suffers from two disadvantages: the distribution of phosphorus over the polymer chain is unknown and the presence of bromine can affect the behaviour of the support, e.g. by quaternization of phosphine with a possibility of cross-linking\textsuperscript{3}. Therefore, we decided to synthesize also a polyiminomethylene) with a phosphine function in each repeating unit (Scheme 2).

Scheme 2

Protection of the carbonyl function in 4-bromoacetoephene, 1, by 1,2-ethanediol gave the acetal 6. Its product of lithiation can be used as a synthon for coupling with many types of reagent. Reaction of this synthon with chlorodiphosphine gave the substituted triphenyl phosphine 7. This compound was hydrolyzed to give 8 which was directly converted to N-formyl[1-(4-diphenylphosphino)-phenyl]ethylamine, 9, via a Leuckart synthesis\textsuperscript{15}. Initial attempts to synthesize 9 through reaction of the Grignard or lithium derivative of 2 with chlorodiphosphine failed. The isocyanide 10 was obtained in a yield of 75—85\% by dehydration of 9 using either phosphorous chloride\textsuperscript{16} or perchloromethyl formate\textsuperscript{17}, both in combination with triethylamine. Direct synthesis of 10 from isocyanide 3 by reaction with butyllithium and chlorodiphosphine failed unsatisfactory results.

The pale-yellow crystals of 10 were moderately soluble in ethanol and diethyl ether, and soluble in tetrahydrofuran, acetone, chloroform and dichloromethane. In chlorinated hydrocarbons slow decomposition was observed. In the infrared spectrum of 10 strong absorptions were visible at 2142 and 1430 cm\textsuperscript{-1} indicative of the isocyanide and phosphine functions. The structures of 10 and its precursors 8 and 9 were supported by elemental analysis, \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{31}P-NMR and mass spectroscopy.

The isocyanide 10 was readily polymerized by treatment with nickel chloride. After isolation and fractionation, polymer 11 was obtained as a light yellow powder. The polymer was soluble in tetrahydrofuran, chloroform, benzene and toluene, and insoluble in the lower alcohols. The intrinsic viscosity of 11 was dependent on the amount of catalyst used: 5 mol % nickel chloride gave a polymer with [\eta] = 0.02 dl/g. Lowering the amount of catalyst to 0.5 mol % increased this value to [\eta] = 0.04 dl/g. Applying the Mark-Houwink equation as determined for poly(1-phenylethyliminomethylene), one calculates a molecular
weight in the range of 5,000–10,000. Usually, a molecular weight of 40,000-50,000 is found after polymerization of other isocyanides under these conditions. The lower values found for 11 might result from steric hindrance of polymerization by the bulky triphenylphosphine group.

**Experimental part**

Proton NMR spectra were obtained on Varian EM 360 and EM 390 spectrometers. The 13C- and 31P-spectra were recorded on a Varian CFT 20 and a Bruker WH 90 spectrometer, respectively. Elemental analyses were carried out by the Elemental Analytical Section of the Institute for Organic Chemistry TNO under supervision of W. J. Buis. NMR chemical shifts, δ, are given in ppm downfield from internal tetramethylsilane; unless otherwise stated.

**Acetal of 4-bromoacetoephene (6).** To 57 g (0.25 mol) of 6 in 200 ml of dry ether was added 200 ml (0.3 mol) of butyllithium in hexane at a temperature of −5°C during two hours. The solution was stirred for another two hours at 0−5°C, during which time a white precipitate was formed. After drying over K₂CO₃; yield 75−85%.

**Poly[1-[4-(diphenylphosphino) phenyl] ethyl iminomethylene] (8).** To a small portion of 7 were added 0.5 ml of formic acid, 0.5 ml of chloroform and 0.54 g) were added 0.5 ml of HCl. The precipitate was collected by filtration and the residue was distilled in vacuo in 150 ml of tetrahydrofuran. The precipitate was dissolved in tetrahydrofuran and added drop by drop to a hundredfold excess of ether. Collecting the solid and drying in vacuo afforded 3.2 g of creamish brown 5b. The calculated composition of 5b is given in Table 1. It was based on the elemental analysis: C 73.80, H 6.23, Br 3.68, N 6.22; IR (KBr): 2000−1700 (mono- and disubst. ar.).

### Table 1

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2 ml of water. This mixture was shaken for 30 minutes, water was decanted and the solution was concentrated. Crystallization from ethanol afforded 0.38 g (80%) of 8; m.p. 106-108°; IR (KBr): 2142.0 ± 0.5 (NC, CO calibration), 2000-1700 (mono- and disubst. arom.), 1617.5 ± 1.5 (N=C, H-,0 vapour calibration), 1580 (arom.), 1475 and 1396 (CH3), 1435 (P-Ph), 825 (1,4-disubst. arom.), 745 and 695 (monosubst. arom.) cm⁻¹; ¹H-NMR (CD3COCD3): δ 4.10 (d, 3H, CH3), 5.05 (q, 1H, CH), 7.3 (br, 14H, arom.), 8.0 (Av, 22 Hz, br, 14H, arom.); ³¹P-NMR (CD3COCD3): δ 4.6 (Av, 50 Hz, br), 36 (Av, 75 Hz, br, intensity is 1/6 of main peak) ppm (relative to 85% H3PO4); the occurrence of the latter peak is neither shown in separate experiments.

The first fraction (1.30 g) was dissolved in 8 ml of an ethanolic solution which contained 9 mg (0.5 mol %) of nickel chloride hexahydrate. The solution was stirred for four days at room temperature and the resulting suspension centrifuged; after decantation of the supernatant liquid the solid was twice suspended in methanol and isolated by centrifugation. Drying in vacuo (30°, 0.01 mm) afforded 1.65 g (70%) of polymer 11 as a light yellow powder. It was dissolved in 10 ml of THF, fractionated over a deactivated silica column and eluted with THF/ethanol (10:1, v/v); yield 1.60 g. The first fraction (1.30 g) was dissolved in 10 ml of THF and added drop by drop to 200 ml of pure methanol, which was stirred rapidly. The resulting suspension was centrifuged and the supernatant liquor decanted. After drying in vacuo (35°, 0.005 mm) 1.19 g of 11 was collected; [r|] = 0.04 dl/g. This polymer was characterized by NMR spectroscopy and elemental analysis.

Acknowledgement

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