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Synthesis, characterization and use of reactive polymers with diisopropylphenylphosphine groups

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Summary

The synthesis of linear and crosslinked polymers starting with 4-(diisopropyl-phosphinyl) styrene is described. Treatment with triphosgene yields the corresponding phosphine dichloride group in the polymers. Using these reactive polymers benzyl alcohol was converted to benzyl chloride at room temperature. The regeneration of the reactive polymers using triphosgene was achieved. The yields of benzyl chloride were in general lower than those previously reported using triphenylphosphine dichloride groups in the polymers. The difference in reactivity between triphenylphosphine dichloride- and diisopropylphenylphosphine dichloride substituted-polymers are discussed with the aid of semi-empirical computer calculations.

Introduction

A polymeric reagent is a polymer with active functional groups available for reactions. These groups are consumed in stoichiometric quantities during the course of a reaction with an added substrate. In some cases the functional groups in the polymers can be regenerated for repeated use, yielding reusable polymeric reagents (1). Polymers containing phosphorus-groups have received considerable attention for application as polymeric reagents, polymeric ligands and polymeric catalysts.

Reported applications of phosphine polymeric reagents include, among others: the Wittig reaction (2), cleavage of ethers (3), reduction of disulphides (4), peptide synthesis (5), conversion of alcohols to halides (6,7,8), primary amides to nitriles (9) and of acids to acid chlorides (10).

Most of the reported phosphorus containing polymeric reagents are based on triphenylphosphine groups (2,3,5-10). Analogous polymer-bound alkylphosphines are expected to show higher reactivity for a variety of chemical transformations due to the greater basicity and nucleophilicity of alkylphosphines (11). Although the study of polymer-bound alkylphosphonium salts as phase transfer catalysts is well established (12), polymer-bound alkylphosphines are reported only by Regen et al.(4). In a publication in 1965 (13) the polymerization of aliphatic vinylphosphonium compounds was tried but with little success.

Here we wish to report on the synthesis of polymers with dialkylphosphine groups by polymerization of appropriate monomers, the further modification of the resulting polymers, and their application as polymeric reagents to the conversion of benzyl alcohol to benzyl chloride.

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Experimental

Synthesis of diisopropylphenylphosphine-functionalized polymers (I)

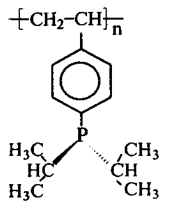
The functionalized monomer p-styryldiisopropylphosphine was obtained via a Grignard-reaction, starting from 4-chlorostyrene (Aldrich) and chlorodiisopropylphosphine (Aldrich) by a slight modification of the methodology described (14). Magnesium (0.206 mol) was pre-activated by stirring under dry nitrogen flux for 16 h. Bromoethane (0.01 mol) was then added dropwise together with 4-chlorostyrene (0.04 mol) in 17 mL of dry tetrahydrofuran (THF) and the reaction maintained between 35-50 °C for 30 min. After cooling to –40 °C, chlorodiisopropylphosphine (0.036 mol) disolved in 25 mL of dry THF was added dropwise in a one hour period. Further treatment and purification of the product was realized according to (14). The functionalized monomer was obtained in 69% yield and its identity was confirmed by ^{1}H NMR (200 MHz, Varian: Gemini 200) and mass spectrometry (Hewlett-Packard 5989A).

Free radical solution homopolymerizations were carried out as described (8) with the exception that diethyl ether was used instead of hexane as precipitating agent. Azo(bis)isobutyronitrile (AIBN) in different amounts was used as initiator. Crosslinked polymers with the same functional groups were obtained by copolymerization of the synthesized phosphine-monomer with divinylbenzene (DVB) in different amounts using 1 mol% of AIBN. Since DVB (Aldrich) is a mixture of 55% DVB and 45% of ethylvinylbenzene isomers, the resulting crosslinked polymers have also different amounts of ethylvinylbenzene co-monomer. The reported contents of DVB in the crosslinked polymers are calculated as pure DVB added taking this fact into account. The synthesis method for these crosslinked polymers is the same as reported previously (8) but using diethyl ether as deswelling agent.

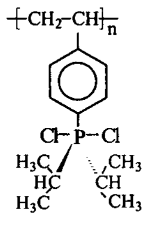
Molecular weights of the homopolymers (I) were determined by membrane-osmometry (Osmomat 090) and by viscosimetry (Ubbelohde-viscosimeters in a Koehler viscosity bath) in chloroform solutions at 25 °C. The Kuhn-Mark-Houwink constants for polystyrene (15) were used for the viscosimetry determinations. The thermal properties were measured by a simultaneous DTA-TG method (Stanton-Redcroft, STA-780) in dry nitrogen flux. A heating rate of 10 K/min and calcinated alumina as reference material were used.

Synthesis and use of diisopropylphenylphosphine dichloride polymers (II)

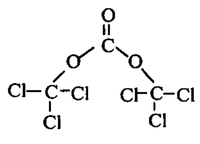
These polymers (II) were obtained by the chemical reaction of the previously synthesized polymers (I) (homopolymers and crosslinked polymers) using triphosgene (III).



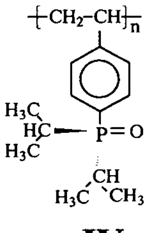
I



II



III



IV

Under dry nitrogen flux approx. 1.0 g of polymer (I) was stirred in 50 mL of dry dichloromethane for 1 h, allowing complete dissolution/swelling. Triphosgene (III) (1.0 mol for every 2.6 moles of phosphine in the polymers) was dissolved in 2 mL of dry dichloromethane and added dropwise to the stirred polymer solution/mixture. The mixture was stirred for 2 h to allow complete conversion of polymer (I) to polymer (II). The obtained polymers (II) (homopolymers and crosslinked ones) were used immediately after preparation in a reaction with benzyl alcohol. For this reaction benzyl alcohol (Aldrich, 1.0 mol for every 1.7 moles of phosphine dichloride in the polymers) was added dropwise to a stirred solution/mixture of the polymer (II) in dichloromethane. The reaction was conducted at room temperature for 1 h. Identification of the reaction products was done by GC-MS (Hewlett-Packard 5890 II/5971) and the yield of benzyl chloride was obtained by integration of peaks of the respective gas chromatograms (GC-FID, Hewlett-Packard 5890 II). The experimental procedures are described in detail (8). After the above reaction with benzyl alcohol, the polymeric reagents (II) were now diisopropylphenylphosphine oxides (IV). In a previous work (8), the efficiency of triphosgene (III) for the regeneration of triphenylphosphine dichloride groups starting with triphenylphosphine oxide polymers, was demonstrated. We tried the same methodology (2 h room temperature, stirred reactions) for the regeneration of the polymeric reagents (II). The completness of the regeneration was investigated indirectly by the repetitive use of the so regenerated polymers (II) in further reactions with benzyl alcohol as a model reaction.

Semiempirical computer calculations

Semiempirical calculations were performed using the SPARTAN 3.5 program in an Indigo XS24 workstation with a R4400 processor. Several semiempirical methods (PM3, AM1, MNDO, SYBIL and STO) were tested for their accuracy in geometry calculations on the following model phosphines: triphenylphosphine, triphenylphosphine oxide, trimethylphosphine and trimethylphosphine oxide, for which X-ray data were available (16). The AM1 method gave the best results, and this method was used for the calculation of geometry and energy of formation of the postulated intermediates for the reaction of benzyl alcohol with diisopropylphenylphosphine dichloride and triphenylphosphine dichloride.

Results and Discussion

Synthesis and characterization of the polymeric reagents

By solution homopolymerization of p-styryldiisopropylphosphine, linear polymers with diisopropylphenylphosphine groups in every repeat-unit were obtained (I), yielding highly functionalized polymers.

Table 1: Molecular weights of the linear polymers (I).

AIBN Mol%	M_η [g/mol]	M_n [g/mol]
1.0	36 200	35 500
1.5	23 500	-
2.5	20 800	18 100

Table 2: Thermal properties of the functionalized polymers (I)

Parameter	0* weight % DVB	4 weight % DVB	7 weight % DVB	15 weight % DVB
T_g [°C]	156	151	167	137
T_{10} [°C]	195	265	177	178
T_D [°C]	439	446	448	445

* Linear polymer (I) prepared with 1 mol% AIBN

The results of molecular weight determinations are shown in Table 1. As expected, we found higher molecular weights for the polymers (I) prepared with lower concentration on AIBN as initiator.

The linear polymers and gels (I) showed good thermal stability (see Table 2).The glass transition temperatures (T_g) are higher than that for polystyrene. Nevertheless, the thermal properties are, in general, lower than those of the corresponding triphenylphosphine functionalized polymers reported (8).

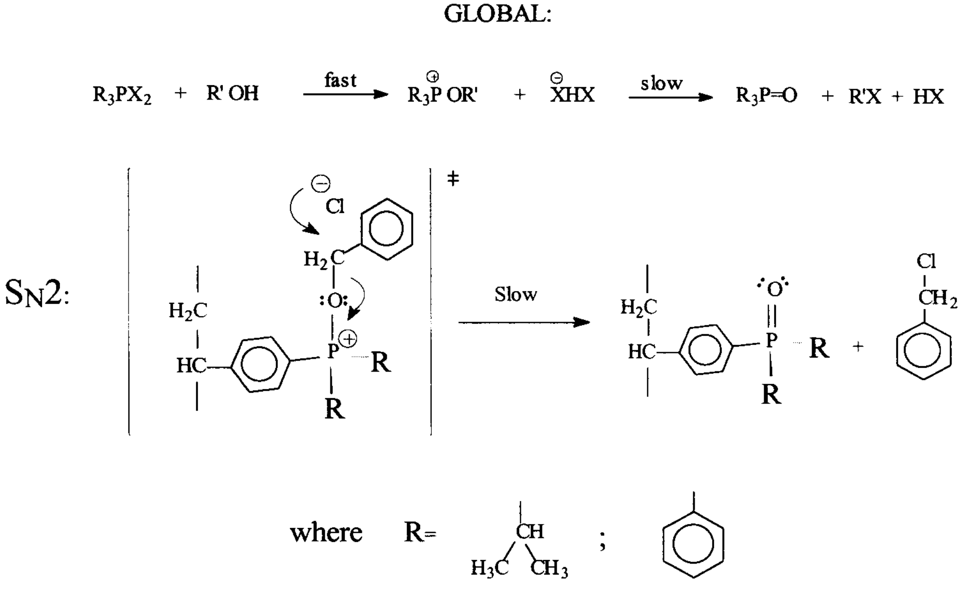
Conversion of benzyl alcohol to benzyl chloride using polymers (II)

After treatment of the polymers (I) with triphosgene (III), the obtained polymers (II) were immediately tested by reaction with benzyl alcohol at room temperature. Table 3 gives the percent yield of benzyl chloride obtained as the %DVB was varied. Although high yields were observed (>50%,original polymers) they were lower than the yields obtained by the use of triphenylphsophine dichloride funtionalized polymers (8). No clear dependence in the reactivity of the polymers with different crosslink densities was observed. After two regenerations of the reactive polymers (II), the capacity for reaction with benzyl alcohol had dropped, a result we had not observed in our previous work (8). Altogether, these results showed that the reactivity of polymeric reagents with triphenylphosphine dichloride and diisopropylphenylphosphine dichloride groups were quite different.

Table 3: Conversion of benzyl alcohol using phosphine dichloride polymers at room temperature.

DVB-Content (weight%)	Benzyl chloride Yield% original polymer		Benzyl chloride Yield% first regeneration		Benzyl chloride Yield% second regeneration	
	II	Ref. (8)	II	Ref. (8)	II	Ref. (8)
0*	51.5	40	45.1	75	29.5	-
7(8[a])	55.7	100	73.1	100	18.0	-
15	57.2	94	35.9	94	38.0	-

* Linear polymer (I) prepared with 1 mol% AIBN ; a - reference (8)



$$R_3PX_2 + R'OH \xrightarrow{fast} R_3\overset{\oplus}{P}OR' + \overset{\ominus}{X}HX \xrightarrow{slow} R_3P{=}O + R'X + HX$$

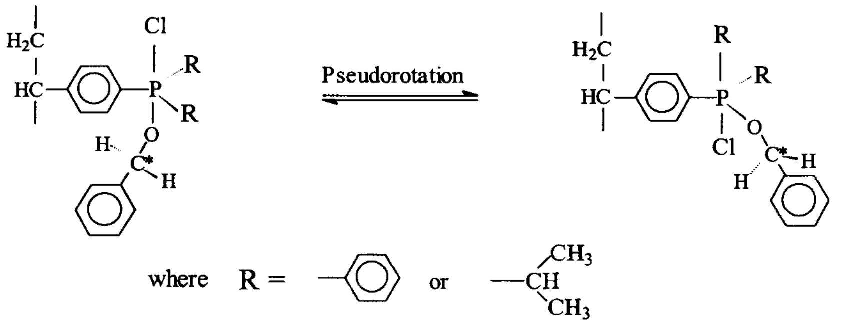
Figure 1: Partial mechanism of the reaction of tertiary phosphine dihalides with benzyl alcohol.

Reaction mechanism and computer calculations

For the reaction of tertiary phosphine dihalides with alcohols, Wiley et al.(17) proposed a 2 step process. In the first step an ionic intermediate is formed in a rapid, irreversible reaction. This intermediate has a tetrahedral phosphonium structure (see Figure 1). In the second, rate-limiting step, the alkyl halide is formed via an S_N2 mechanism. In this step the phosphonium moiety acts as a leaving group and leads to the corresponding phosphine oxide (Figure 1). If we compare the phosphines we studied, namely, polymeric triphenylphosphine dichloride (8) and polymeric diisopropylphenylphosphine dichloride (this work), we find that they yield different leaving groups in this reaction: the first yields a tri aromatic phosphine oxide while the second yields a dialkyl monoaromatic phosphine oxide. From general chemistry it is known that the weaker the base the better leaving groups they are. Since diisopropylphenylphosphine is a stronger base than triphenylphosphine (11), the oxide from the former should act as a poorer leaving group; this would lead to a lower reaction rate, resulting in lower yields of alkyl chlorides at constant reaction times than the yields obtained with triphenylphosphine groups.

Alternatively, for the chlorination of alcohols in non-polar solvents using the system triphenylphosphine/CCl_4, Weiss and Snyder (18,19) proposed a pentavalent phosphine intermediate in which the alkoxy-radical and halogen occupies apical positions in a trigonal bipyramid (see V in Figure 2). The decomposition of this intermediate to

V **VI**



R =	V- Isomer d (Cl- C*)	V- Isomer ∠ (Cl-P-C*)	VI- Isomer d (Cl- C*)	VI- Isomer ∠ (Cl-P-C*)	ΔE
Phenyl	4.94 Å	156.5 °	2.91 Å	69.7 °	1.01 KJ/Mol
Isopropyl	5.07 Å	155.4 °	2.93 Å	67.5 °	3.35 KJ/Mol

Figure 2: Semiempirical calculations of the more stable isomeric forms for the proposed five-coordinate phosphorus intermediates.

products involves a four centered concerted process in which the halogen internally attacks the carbon atom (C^* in Figure 2) of the alkoxy-radical. Prior to this, the intermediate should rearrange by a series of pseudorotation-steps to an appropriate structure, in which halogen and C^* are closer to each other. We performed semiempirical computer calculations on all possible isomers of five-coordinated phosphorus compounds with phenyl and isopropyl radicals (see Figure 2). We have found that the more stable isomeric forms (V and VI) have an energy difference of only 1.01 KJ/mol for the phosphines with phenyls and 3.35 KJ/mol for the phosphines with isopropyl groups. This tendency shows that more energy is required for the pseudorotation steps in the case of the diisopropylphenylphosphine intermediate and therefore the reaction of this phosphine compound with an alcohol should be slower than the corresponding reaction with a triphenylphosphine compound. Nevertheless we should take into account that for room temperature reactions an energy difference of about 2 KJ/mol may be neglected. A parallel can be drawn to the well studied Wittig-reaction: Maryanoff et al.(20,21) pointed out that in the case of nonstabilized ylids, for the formation of a pentavalent oxaphosphetane intermediate alkylated phosphine ylids react faster than aromatic ones, but for the rate limiting decomposition of oxaphosphetane to alkene and phosphine oxide, they report 2–10 times slower decomposition of tributylphosphine-oxaphosphetane than the decomposition of the corresponding triphenylphosphine-intermediate.

In conclusion, we find in the literature evidence (17,21) that make us believe that polymeric diisopropylphenylphosphine dichloride may react more slowly with alcohols than polymeric triphenylphosphine dichloride. The kinetics of these reactions are currently under investigation in our group.

Acknowledgments

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