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Studies of structures and concentration of active species in vinyl anionic polymerization by phosphorus end-capping

I. *n*-Butyllithium – determination of concentration and impurities

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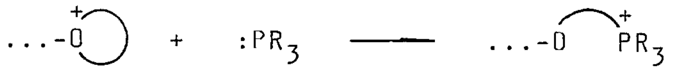
SUMMARY

It has been shown that chlorodiarylphosphines react quantitatively with carbanions giving the corresponding phosphines as the only products. On this basis, the method of determination of carbanions concentration by ^{31}P-NMR has been developed. In the present paper the determination of n-C_4H_9Li concentration in the presence of other anions is described.

INTRODUCTION

In our previous papers, devoted to the determination of the structures of active species, we developed functionalization of the chain ends with phosphorus containing compounds. The phosphorus atom at the end of the chain is the only one giving the ^{31}P-NMR signal from the entire macromolecule. In this way we determined structures of the growing ends in the cationic polymerization of cyclic ethers and cyclic acetals (BRZEZINSKA et al. 1980) by using aliphatic or aromatic phosphines:



(1)

This reaction is fast enough to virtually stop the propagation at the moment of phosphine addition (MATYJASZEWSKI and PENCZEK 1981). With aliphatic phosphines it is sufficiently irreversible even for cyclic acetals. Moreover, the method is sensitive enough to distinguish, for instance, between 4,5- and 7-membered rings engaged in oxonium ions at the end of the chain.

We have also developed similar technique in the anionic ring-opening polymerization. After trying a number of phosphorus containing compounds, we adopted reaction of anions with diphenyl chlorophosphate. This has successfully been used in anionic polymerization

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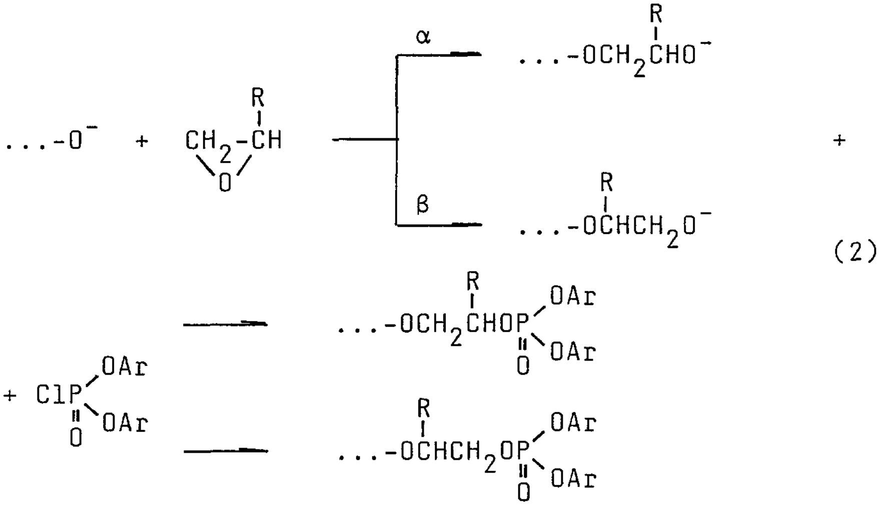
*To whom offprint requests should be sent of cyclic ethers and esters (β-propiolactone and ε-caprolactone) (SOSNOWSKI et al. 1984, PENCZEK and SLOMKOWSKI 1987), sulfides and cyclosiloxanes (SOSNOWSKI et al. 1984, PENCZEK and SLOMKOWSKI 1987) and more recently cyclic carbonates (KUHLING et al. 1989, KEUL et al. 1990). The high sensitivity of ^{31}P-NMR to the chemical environment of the studied P-atom allowed, for instance, to determine the proportions of the α and β ring openings in the polymerization of cyclic ethers:



(2)

In this paper we describe our first results of the application of the same concept to the vinyl polymerization, namely for carbanions. We have chosen, as the first system, merely n-butyllithium.

Direct determination of $n\text{-}C_4H_9Li$ in solution and in the presence of other anions is important for studies of anionic polymerization initiated by $n\text{-}C_4H_9Li$. Moreover, as it will become apparent further from the text, the elaborated method allows to determine small amounts of ionic impurities (like $n\text{-}C_4H_9OLi$) in $n\text{-}C_4H_9Li$ solutions.

When this work was very much advanced, a paper appeared (LINDSELL et al. 1990), describing conversion of the living anionic polybutadiene into the polymeric phosphine and eventually into the quaternary phosphonium salts, in order to study interactions of macromolecules ended with stable ion-pairs.

EXPERIMENTAL

n-Butyllithium ($n\text{-}C_4H_9Li$) (Merck) (~15% wt. solution in n-hexane) was used as supplied. The concentration of n-C_4H_9Li was determined independently by GILMAN method (GILMAN and CARTLEDGE, 1964) and found equal to 14.05% wt.

Chlorodiphenylphosphine ($ClP(C_6H_5)_2$) (Merck) was purifed by vacuum distillation (b.p.=80-81°/0.1mmHg).

Trimethylchlorosilane ($ClSi(CH_3)_3$) (POCh, Poland) was purified by distillation (b.p.=56-57°/760mmHg).

Solvents (tetrahydrofuran, n-hexane) were purified according to known methods and finally dried over sodium-potassium alloy.

Reaction between n-C_4H_9Li and $ClP(C_6H_5)_2$ was carried out in ampoules closed with Rotaflo® stopcocks in vacuum. n-C_4H_9Li solution was transferred into an ampoule by a syringe, under argon. After degassing and closing an ampoule in vacuum, $ClP(C_6H_5)_2$ was introduced from a calibrated tube trough Rotaflo® stopcock and reaction was allowed to proceed for 24h at -78°. After filling the ampoule with dry argon, the content was diluted with equal volume of THF to homogenize the reaction mixture and the sample was transferred to the NMR tube. Reaction with $ClSi(CH_3)_3$ was carried out essentially in the same way, with silane distilled directly into the ampoule.

^1H- and ^{31}P-NMR spectra were recorded with Bruker AC-200 apparatus.

RESULTS AND DISCUSSION

Several groups of organophosphorus compounds containing the reactive Cl-P bond, have been tested in order to select the capping agent, reacting with carbanions quantitatively and without side-reactions. These included:

$ClP(O)(OAr)_2$ - diaryl chlorophosphates

$ClP(O)(Ar)_2$ - chlorodiarylphosphine oxides

$ClPAr_2$ - chlorodiarylphosphines

Analysis of ^{31}P-NMR spectra of the products led to conclusion, that in reaction of diaryl chlorophosphates with carbanions, not only the Cl-P bond is broken but also the P-OAr bond becomes affected. Thus, the reaction course is not well defined and reaction could not be used for quantitative determination of n-C_4H_9Li.

Chlorodiarylphosphine oxides also give side-reactions, one of the identified side-products is the corresponding pyrophosphinite: $Ar_2P(O)OP(O)Ar_2$.

On the contrary, when chlorodiphenylphosphine was used as a capping agent, only two narrow, well separated signals were observed in resulting ^{31}P-NMR spectra: signal of the unreacted excess of chlorodiphenylphosphine at 82.2 ppm δ and signal of n-butyldiphenylphosphine at -15.9 ppm δ.

This indicate, that the only reaction proceeding in the system is reaction (3)

$$n\text{-}C_4H_9Li + ClP(C_6H_5)_2 \longrightarrow n\text{-}C_4H_9P(C_6H_5)_2 + LiCl \quad (3)$$

Using a known excess of chlorodiphenylphosphine and comparing the intensities of signals of unreacted excess of the capping agent and product (from integration), one can calculate the concentration of n-butyldiphenylphosphine formed. In order to confirm, that reaction (3) proceeds quantitatively, i.e. that concentration of alkyldiarylphosphine formed is indeed equal to the concentration of carbanions originally present in the reaction mixture, the values determined from ^{31}P-NMR spectra were compared with concentrations of $n\text{-}C_4H_9Li$ found from GILMAN method (GILMAN and CARTLEDGE 1964).

TABLE 1.
Comparison of the known concentration of $n\text{-}C_4H_9Li$ with a concentration determined on the basis of the amount of $n\text{-}C_4H_9P(C_6H_5)_2$ formed (^{31}P-NMR). End-capping performed with ~2 fold excess of $ClP(C_6H_5)_2$ at -78°, during 24h. ^{31}P-NMR spectra recorded in n-hexane/THF/C_6D_6 solvent (~2/1/1 vol.).

$[n\text{-}C_4H_9Li]$ known* mol·l^{-1}	$[n\text{-}C_4H_9Li]$ determined from $[n\text{-}C_4H_9P(C_6H_5)_2]$ in ^{31}P-NMR mol·l^{-1}
0.141	0.150
0.145	0.159
0.178	0.182
0.193	0.207

*) based on the results of analysis by GILMAN method

Concentrations determined from ^{31}P-NMR spectra are slightly higher, nevertheless the results indicate. that reaction (3) proceeds quantitatively and the correct values of carbanion concentrations are obtained within the experimental error by the used method.

Only one signal was observed for the product of reaction between the commercial $n\text{-}C_4H_9Li$ solution with $ClP(C_6H_5)_2$. It is known, however, that these solutions are contaminated with n-C_4H_9OLi, LiOH and LiH.

It was independently shown, that n-C_4H_9OLi reacts quantitatively with $ClP(C_6H_5)_2$ and only signal at 112.1 ppm δ is observed in ^{31}P-NMR spectrum.

$$\text{n-}C_4H_9OLi + ClP(C_6H_5)_2 \longrightarrow \text{n-}C_4H_9OP(C_6H_5)_2 \qquad (4)$$

In order to prove, that n-C_4H_9OLi, if present in solutions of n-C_4H_9Li in sufficient concentration, would indeed give a separate signal, controlled amounts of n-C_4H_9OH were added to n-C_4H_9Li solutions prior to capping with $ClP(C_6H_5)_2$. In this case, part of n-C_4H_9Li should be converted into n-C_4H_9OLi, according to scheme (5):

$$\text{n-}C_4H_9Li + \text{n-}C_4H_9OH \longrightarrow \text{n-}C_4H_9OLi + \text{n-}C_4H_{10} \qquad (5)$$

The typical ^{31}P-NMR spectrum of a mixture of n-C_4H_9Li and n-C_4H_9OH, capped with $ClP(C_6H_5)_2$, is shown in Fig. 1.

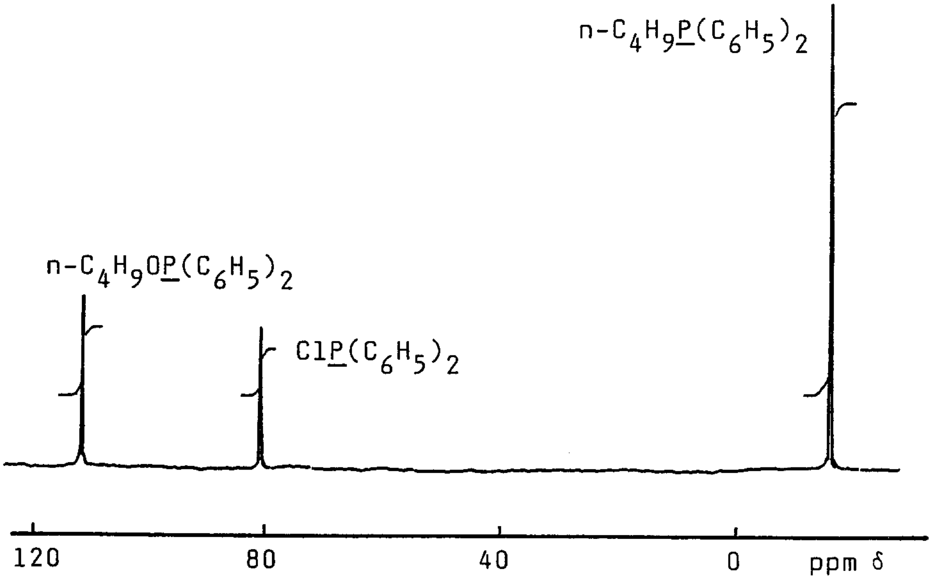


Fig.1. $^{31}P\{^1H\}$NMR spectrum (81.018 MHz) of the reaction mixture of n-C_4H_9Li and n-C_4H_9OH capped with $ClP(C_6H_5)_2$ in n-hexane/THF/C_6H_6 solution. $[\text{n-}C_4H_9Li]_o = 0.26\ mol \cdot l^{-1}$, $[\text{n-}C_4H_9OH]_o = 0.05\ mol \cdot l^{-1}$, $[ClP(C_6H_5)_2]_o = 0.34\ mol \cdot l^{-1}$

Indeed, two signals at -15.9 ppm δ ($n\text{-}C_4H_9P(C_6H_5)_2$) and at 112.1 ppm δ ($n\text{-}C_4H_9OP(C_6H_5)_2$) are observed separately, together with the signal of unreacted excess of $ClP(C_6H_5)_2$, allowing the determination of the concentration of both components.

In Table 2, the known values of concentrations of $n\text{-}C_4H_9Li$ ($[n\text{-}C_4H_9Li] = [n\text{-}C_4H_9Li]_0 - [n\text{-}C_4H_9OH]_0$) and $n\text{-}C_4H_9OLi$ ($[n\text{-}C_4H_9OLi] = [n\text{-}C_4H_9OH]_0$) are compared with these determined from ^{31}P-NMR spectra.

TABLE 2.

Comparison of the known concentrations of $n\text{-}C_4H_9Li$ and $n\text{-}C_4H_9OLi$ with concentrations determined on the basis of amounts of $n\text{-}C_4H_9P(C_6H_5)_2$ and $n\text{-}C_4H_9OP(C_6H_5)_2$ formed (^{31}P-NMR).

End-capping performed with ~2-fold excess of $ClP(C_6H_5)_2$ -78°, 24h, ^{31}P-NMR spectra recorded in n-hexane/THF//C_6H_6 solvent (~2/1/1 vol).

$[n\text{-}C_4H_9Li]$, mol·l^{-1}		$[n\text{-}C_4H_9OLi]$, mol·l^{-1}		$\frac{[n\text{-}C_4H_9Li]}{[n\text{-}C_4H_9Li]+[n\text{-}C_4H_9OLi]}$	
known*	determin.	known**	determin.	known	determin.
0.126	0.115	0.0192	0.0115	0.132	0.091
0.225	0.227	0.0980	0.111	0.303	0.328
0.172	0.194	0.0957	0.118	0.357	0.378

*) $[n\text{-}C_4H_9Li]$ known = $[n\text{-}C_4H_9Li]_0 - [n\text{-}C_4H_9OH]_0$

**) $[n\text{-}C_4H_9OLi]$ known = $[n\text{-}C_4H_9OH]_0$

Results show, that in the mixture of $n\text{-}C_4H_9Li$ and $n\text{-}C_4H_9OLi$, concentrations of both components may be determined with a reasonable accuracy, using the applied method, providing that the concentration of $n\text{-}C_4H_9OLi$ is not below of a certain level, depending on the NMR apparatus used.

The absence of a signal corresponding to $n\text{-}C_4H_9OLi$ in the reaction products of $n\text{-}C_4H_9Li$ with $ClP(C_6H_5)_2$ (cf. Table 1) may indicate, that concentration of $n\text{-}C_4H_9OLi$ present as an impurity in the analysed sample of $n\text{-}C_4H_9Li$, was below detection limit of the apparatus we used.

In order to confirm this assumption, $n\text{-}C_4H_9Li$ sample was hydrolysed with 5-fold excess of water at -78°. Upon hydrolysis, $n\text{-}C_4H_9Li$ gives n-butane, while $n\text{-}C_4H_9OLi$ leads to n-butanol. The content of $n\text{-}C_4H_9OH$ in hydrolysate was determined by glc. By this method it was shown, that the content of $n\text{-}C_4H_9OLi$ is indeed low and corresponds to merely 0.85% mol with respect to $n\text{-}C_4H_9Li$.

The low content of $n\text{-}C_4H_9OLi$ in $n\text{-}C_4H_9Li$ was confirmed additionally by analysing ^1H-NMR spectra of the products of reaction between $n\text{-}C_4H_9Li$ and $(CH_3)_3SiCl$.

$n\text{-}C_4H_9Li$ reacts with $(CH_3)_3SiCl$, according to a scheme:

$$n\text{-}C_4H_9Li + ClSi(CH_3)_3 \longrightarrow n\text{-}C_4H_9Si(CH_3)_3 + LiCl \quad (6)$$

Reaction proceeds quantitatively, as shown by the reasonably good agreement between the known concentrations of $n\text{-}C_4H_9Li$ and concentrations calculated on the basis of the intensity of $n\text{-}C_4H_9Si(CH_3)_3$ groups signal appearing at -0.14 ppm δ (unreacted excess of $(CH_3)_3SiCl$ gives a signal at 0.27 ppm δ).

The known concentration of $n\text{-}C_4H_9Li$ was equal to 0.141 $mol \cdot l^{-1}$, whereas we determined: 0.148; 0.149; 0.153; and 0.169 $mol \cdot l^{-1}$. Thus, the best result is within 5% of the measured value.

Additional small signals appear at -0.02 ppm δ. Based on the spectra of the corresponding model compounds it was shown, that in this region signals of $n\text{-}C_4H_9OSi(CH_3)_3$ (product of reaction of $n\text{-}C_4H_9OLi$ with $(CH_3)_3SiCl$) and of $(CH_3)_3SiOSi(CH_3)_3$ (product of reaction of LiOH with $(CH_3)_3SiCl$) overlap. Thus, only the sum of $n\text{-}C_4H_9OLi$ and LiOH concentrations can be obtained from the integration of the signals. The resulting value is equal to 2.25% mol with respect to $n\text{-}C_4H_9Li$.

The results of analysis by glc and ^1H-NMR confirm, that the content of $n\text{-}C_4H_9OLi$ in the analysed sample of $n\text{-}C_4H_9Li$ is indeed low (~1% mol).

This work was performed with a relatively concentrated $n\text{-}C_4H_9Li$ solutions. In the actual polymerization concentration of anions can be at least one order of magnitude lower. Methods of enhancing sensitivity will be discussed in the next paper of this series.

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