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NMR STUDIES OF ORGANOMETALLIC COMPLEXES AND THEIR ETHERATES

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INTRODUCTION

The complexes resulting from the association of a nucleophilic organo-alkali compound with an organometallic Lewis acid of Groups III, IIA or IIB are often used as catalysts for the polymerization of various methacrylic esters. They were found to play an important role with respect to the stereoregularity of the resulting polymer[1,2].

In this sense, the polymerization of methyl methacrylate[3], methacrylonitrile[4] and styrene[5] in the presence of the complexes $BuLi \cdot Et_2Zn$ or $EtLi \cdot Et_2Zn$ as catalyst, has recently been examined from the double point of view of the reaction kinetics and the tactilities of the polymer.

A complete bibliographic review of the chemistry of these *ate* complexes was published recently by Tochtermann[6].

With regard to the composition of these complexes, it is noted that when the Lewis acid belongs to Group III, the ratio 1 : 1 is always observed *e.g.*, $LiAl(C_2H_5)_4$ or $LiB(C_6H_5)_4$; moreover these complexes can be isolated as crystalline substances.

When the acidic organometallic compound belongs to Group II, the metal is able to accept more than one ligand in order to complete its valence shell; consequently, these complexes are more diverse in composition. Besides the 1 : 1 complexes, such as $NaZn(C_2H_5)_3$ and $LiZn(C_6H_5)_3$, which are the most frequently encountered, 2 : 1 complexes have been described by some authors; *e.g.*, $(LiMe)_2 \cdot Me_2Zn \cdot 1\ Et_2O$[7].

In a recent paper[8], the existence of species of the form $Li_2M(CH_3)_4$ and $Li_3M(CH_3)_5$ in ethereal solution was reported by Brown *et al.* (M = Zn and Mg). With ^7Li and ^1H in NMR spectroscopy (at low temperatures where the alkyl exchange reactions are slower) distinct signals have been detected corresponding to the various species present in the solution.

Wittig also reported the existence of $(LiC_6H_5)_3 \cdot [Zn(C_6H_5)_2]_2 \cdot 4$-dioxan. The ethyllithium-diethylzinc complex can only be isolated as an oily product of doubtful purity. On the other hand, ethyllithium-diethylzinc complexes have been used for the polymerization of methyl methacrylate, methacrylonitrile and styrene, in toluene solution or in mixed solvents, *e.g.*, toluene containing small amounts of dioxan, diethylether, dimethoxyethane or tetrahydrofuran (THF). It is therefore of interest to determine accurately the composition of these lithium-zinc alkyl complexes in the reaction conditions in which they are used; NMR spectroscopy was used for this purpose. This method enables not only an eventual complex formation between ethyllithium and diethylcadmium or diethylmercury in various reaction media to be disclosed, but also the number of moles of ether effectively coordinated with these complexes to be estimated.

RESULTS AND DISCUSSION

The nuclear magnetic resonance spectra of the initial reagents were described previously in the literature.

For ethyllithium[9] diethylzinc and diethylcadmium[10], at 60 Mc the methylic triplet and the methylenic quadruplet are well separated and the position of the CH_2 signal is strongly dependent on the electronegativity of the adjacent metal atom. However, in the case of diethylmercury where the weak electropositive metal is bonded covalently to the carbon atom, the methylic and methylenic absorptions can no longer be distinguished; nevertheless, their positions can be easily calculated from the satellite peaks due to unlike couplings of ^{199}Hg with the methylic and methylenic protons, respectively[11].

The NMR spectrum of a solution containing a mixture of two organometallic compounds bearing identical alkyl groups often results in the coalescence of the individual resonances into fused peaks absorbing at the average chemical shift positions as a consequence of a fast exchange of the alkyl groups from one site to the other. A linear relation then exists between the mean observed resonance and the concentration ratio expressed in terms of the number fraction of alkyl groups belonging to one of the metals. When the exchange reaction proceeds more slowly, broadening of the mean signals is observed. If no exchange occurs or if it proceeds very slowly, separated signals characteristic of the pure compounds are observed[12].

When the two organometallic derivatives, not only exchange their alkyl groups rapidly through some electron-deficient transient species but moreover associate into a mixed stable compound, the linear relation vanishes on account of the formation of a third organometallic compound in the solution. The largest deviation will occur for a ratio of the compounds corresponding to the actual composition of the complex.

In the study of the reaction between ethyllithium and the ethyl derivatives of Group II_B, the three cases mentioned above were successively encountered.

Formation of organometallic complexes

$EtLi+Et_2Hg$. In the NMR spectrum of a benzene solution of ethyllithium and diethylmercury there is superposition of the signals characteristics of the pure substances, but after the addition of minute amounts of THF to the mixture, the individual signals are no longer recognizable due to a large broadening resulting from an acceleration of the exchange reaction.

$EtLi+Et_2Cd$. The spectrum of a mixture of ethyllithium and diethylcadmium appears as the spectrum of a single substance.

An investigation of this system in benzene solution was made to establish whether the two reagents exchange their alkyl groups or associate into a mixed compound. Therefore the overall concentration of the two derivatives was kept constant but their ratio progressively varied.

In Fig. 1, where the chemical shifts of the methylic and methylenic protons

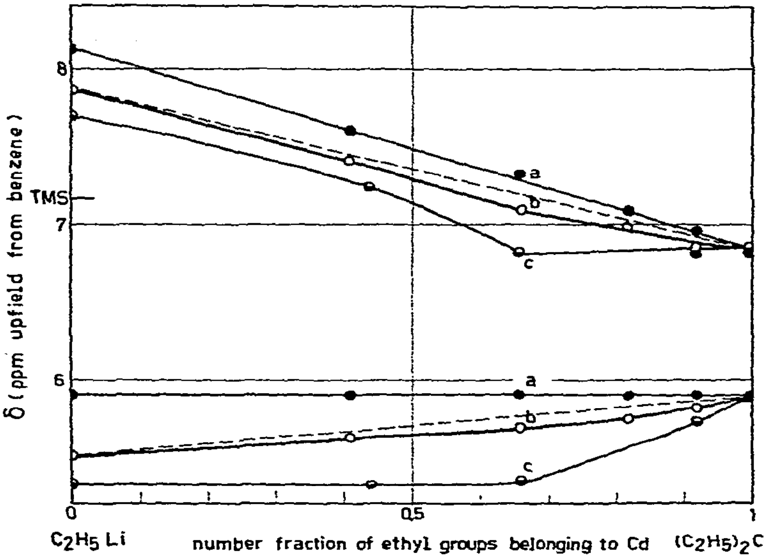

Fig. 1. Influence of the concentration ratios on the NMR resonance signals. (a), EtLi+Et_2Cd in C_6H_6; (b), EtLi+Et_2Cd in C_6H_6+Et_2O; (c), EtLi+Et_2Cd in C_6H_6+THF.

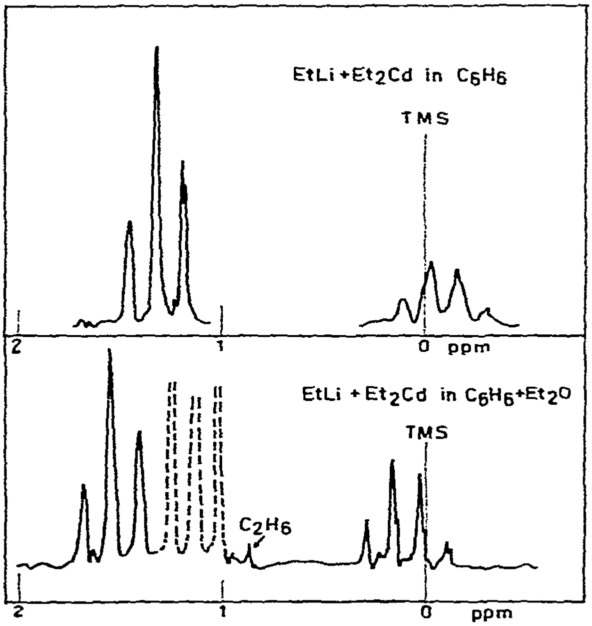

Fig. 2. NMR spectrum of a mixture of ethyllithium–diethylcadmium in: (a), C_6H_6; (b), C_6H_6–Et_2O.

(expressed in ppm upfield from benzene) are plotted against the number fraction of ethyl groups belonging to cadmium, it can be deduced from the linear relation (curve a) that C_2H_5Li and $(C_2H_5)_2Cd$ only exchange their alkyl groups fast enough to cause the coalescence of the individual signals. In Fig. 2, showing the spectrum of a mixture of ethyllithium and diethylcadmium in benzene, it can be seen, however, that the mean quadruplet is rather broad; this indicates that, although the exchange reaction is rapid, the time of residence of an ethyl group in one site is still too long to give a very sharp mean quadruplet.

By comparing the observed line shape with the theoretical curves calculated by Gutowsky and Holm[12] for increasing exchange rate between two sites of equal population, the mean time that an ethyl group spends on a metal before exchanging, can be estimated (the upper limit being $\tau = 1/\pi(\nu_A^0 - \nu_B^0) = 0.004$ sec and the lower one $0.5/\pi(\nu_A^0 - \nu_B^0) = 0.002$ sec). $(\nu_A^0 - \nu_B^0)$ represents the chemical shifts separation between the center of the quadruplet of C_2H_5Li and $(C_2H_5)_2Cd$ *i.e.*, 78 cps.

By adding small amounts of diethylether or THF (nearly four times the concentration of the organometal) a strong sharpening of the methylenic quadruplet is observed (Fig. 2). The formation of an *ate* complex accounts for the deviations from linearity; this is particularly pronounced in the presence of THF (curves b and c, Fig. 1) and the formation of a 1/1 lithiumtriethylcadmiate is quite obvious. In both cases, metal precipitates rapidly after the addition of the oxygen-compound, the carbon–cadmium bond becoming less stable in the presence of ethyllithium.

On the addition of a small amount of dioxan to a benzene solution of the two substances, a white precipitate is immediately formed; it contains more lithium than cadmium equivalents. It is very likely a mixture of the dioxanates of ethyllithium and of lithiumtriethylcadmiate, the diethylcadmium remaining in solution. The precipitate turns rapidly brownish-grey; a similar phenomenon has already been reported by Wittig *et al.*[13] in their descriptions of the preparation of lithiumtriphenylcadmiate.

$EtLi + Et_2Zn$. It is possible, using the same method, to ascertain whether the mixed compound formed in solution between EtLi and Et_2Zn is actually a 1 : 1 complex (Fig. 3). This is in fact the case in pure benzene as well as in a mixed raction medium

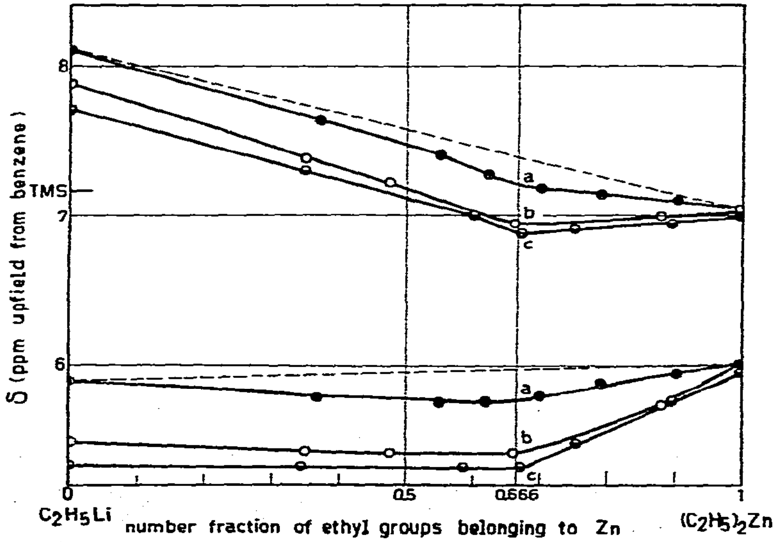

Fig. 3. Influence of the concentration ratios on the NMR resonance signals. (a), $EtLi + Et_2Zn$ in C_6H_6; (b), $EtLi + Et_2Zn$ in $C_6H_6 + Et_2O$; (c), $EtLi + Et_2Zn$ in $C_6H_6 + THF$.

of benzene containing small amounts of ether or THF. The spectrum consists of a single triplet and a single quadruplet all along the scale of the concentration ratios, *i.e.*, a fast exchange of ethyl groups takes place between the lithiumtriethylzincate and its two components.

It is therefore impossible to determine, from the spectrum, any equilibrium constant for the formation of the complex. In any case, the reaction must be very complex and involve several stages, at least in benzene in which lithium alkyl is present in hexameric form, while the final *ate* complex forms high molecular weight aggregates as reported by Hein and Schramm[14]. The calculation of an equilibrium constant, if it were possible, would likely be meaningless.

Coordination of ethers on organometallic derivatives

The shifts of the methylic and methylenic signals of organometallic ethyl compounds have been followed as a function of the amount of ether, the concentration of organometallic compounds being kept constant. For a definite value of the molar ratio (complex)/(ether), a break in these diagrams corresponds to the number of moles of ether that coordinate one mole of organometallic compound. The values of the concentration ratio were deduced from the integrated areas of the resonance signals corresponding to each compound.

In the presence of small amounts of diethylether or THF, no change in the resonance signals of diethylzinc and diethylcadmium can be detected. This may be ascribed to the very weak complexing ability of these two ethers towards diethylzinc[15] and diethylcadmium; it must be remembered also that these two derivatives are already monomeric in benzene.

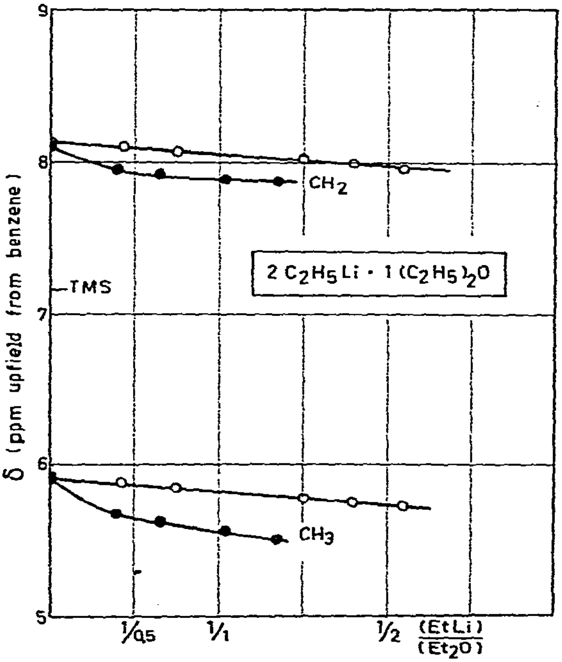

Fig. 4. Influence of the addition of diethylether (●) and of phenylmethylether (○) on the chemical shifts of the CH_3- and CH_2-protons of EtLi: 0.5 mole l^{-1}. Solvent, C_6H_6.

On the other hand, diethylether and THF have a very marked influence on the signals of ethyllithium in benzene; a diagram of the shifts of these signals as a function of the diethylether concentration, shows a break for a molar ratio EtLi/Et_2O equal to 2:1. This result is in agreement with the structure proposed by Eastham for BuLi in hexane in the presence of ether: a solvated dimer, $Et_2O\cdot(BuLi)_2$[16].

In contrast, the addition of increasing amounts of anisole to a benzene solution of ethyllithium affects only very slightly the CH_3 and CH_2 absorption of the organolithium compound and causes no break in the evolution of these values (Fig. 4). Moreover there is no shift in the resonance signal of the methylic protons of the ether. This can be attributed to a negligible coordination of the aromatic ether on ethyllithium.

In the same way, the coordination of one mole of diethylether, one mole of dimethoxyethane and two moles of THF, respectively, per mole of $LiZn(C_2H_5)_3$ may be assumed from Figs. 5 and 6. In these cases the role of ether is not only to coordinate the organometallic derivative but also to depolymerise the ethyllithium hexamer or the $[LiZn(C_2H_5)_3]_n$ in less associated or unassociated aggregates.

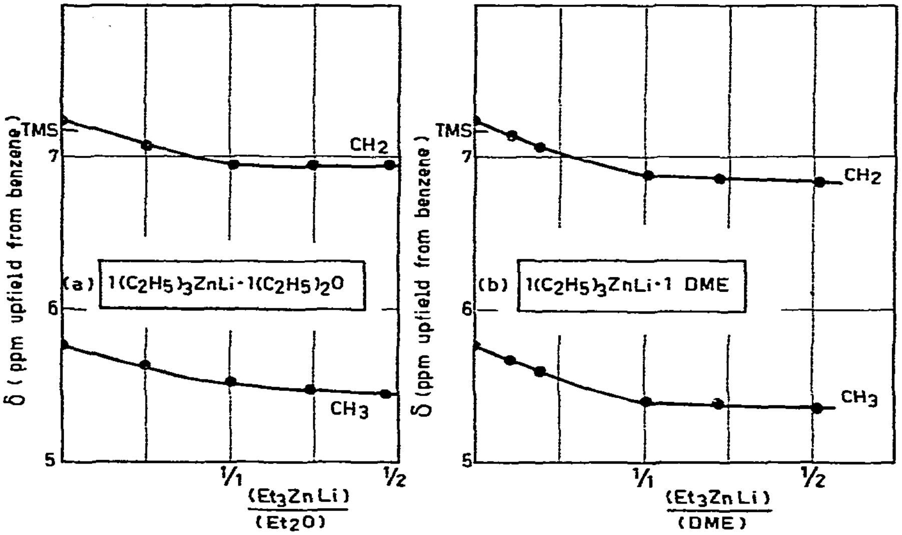

Fig. 5. Influence of the addition of diethylether (a) and of dimethoxyethane (b) on the chemical shifts of the CH_3- and CH_2-protons of lithiumtriethylzincate.

To check the eventuality of an isolatable solvated complex of such composition ($Et_3ZnLi\cdot2$ THF), ethyllithium was mixed with excess of diethylzinc and THF in benzene solution. Removal of the volatile compounds at 25° under vacuum left an oil containing the three components in a mole ratio, 1:1:1.7. The NMR spectrum of this tetrahydrofuranate in benzene is identical with that obtained for a benzene solution of $LiZn(C_2H_5)_3$ and THF in the same ratio.

Finally, the influence of an increasing amount of THF on a benzene solution of ethyllithium–diethylcadmium in the ratio 1:1 has been studied. As stated above, these two compounds only exchange their alkyl groups in pure benzene; the presence of THF is, however, necessary for the formation of a stable 1:1 complex between

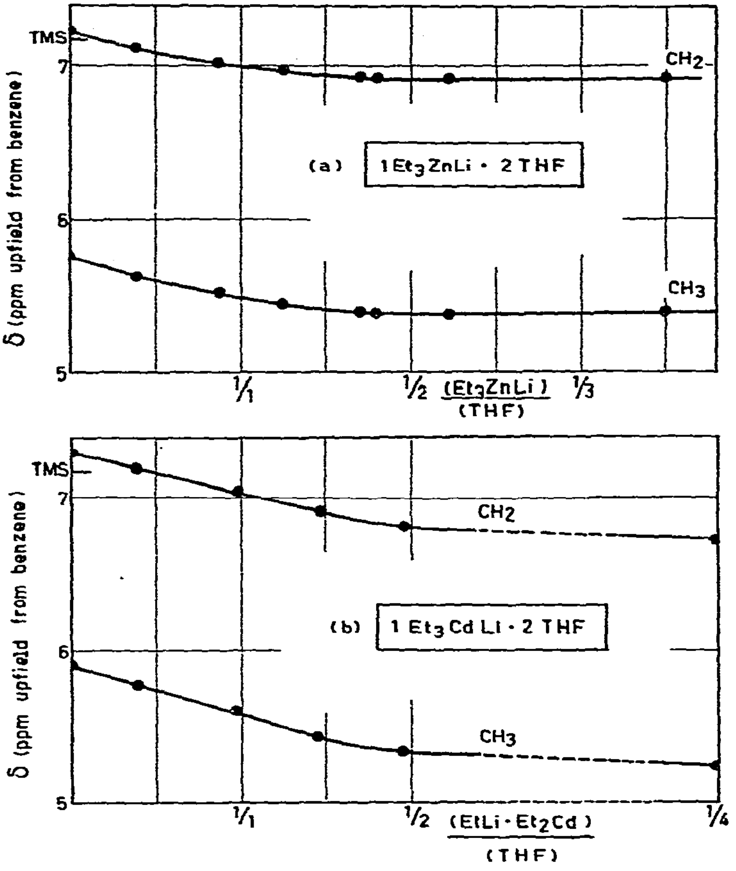

Fig. 6. Influence of the addition of THF on the chemical shifts of the CH_3- and CH_2-protons of: (a), lithiumtriethylzincate; (b), lithiumtriethylcadmiate. Solvent, C_6H_6; concentration of complex, 0.5 mole l^{-1}.

them. From Fig. 6, it can be seen that the complex is solvated by two moles of THF; the further addition of ether has no significant effect on the chemical shifts of the methylic and methylenic protons.

It should be noted that in all cases, the spectra consist of fused sharp signals, for the resonance of the various ethers (Et_2O, THF, DME) as well as for the triplet and quadruplet of the organometallic ethyl complex. If it is assumed that the values of the signals observed are the arithmetic mean of those for complexed and uncomplexed species, equilibrium percentages of the species could be calculated for various initial concentrations. However, any attempt to calculate an equilibrium constant for the solvation of the complex has resulted in unreliable values. In fact, the actual degrees of association in benzene of Et_3ZnLi and of solvated Et_3ZnLi, and, consequently, the nature of the equilibria involved in these reactions, are unknown.

EXPERIMENTAL

Preparation of compounds

Ethyllithium was prepared by the method of Schlenck and Holtz[17] by reacting diethylmercury with a fine lithium dispersion in benzene at 25° for 24 h. The product was recrystallized in an argon atmosphere and dissolved in fresh, dry benzene. The solutions are kept under inert atmosphere in flasks provided with a vacuum stopcock and a rubber cap.

Diethylzinc was obtained according to the method of Noller[18] by reacting a mixture of ethyl bromide and ethyl iodide with a zinc–copper couple[19] in an inert atmosphere.

Diethylcadmium was prepared under argon from ethylmagnesium bromide and anhydrous cadmium bromide.

Diethylmercury was prepared similarly from ethylmagnesium bromide and mercuric bromide.

The hydrocarbon *solvents* were dried over calcium hydride and the ethers over butyllithium and were distilled under high vacuum before use. Argon was purified by bubbling through a trap filled with butyllithium in dodecane.

Analyses

The solution containing both ethyllithium and diethylzinc, or ethyllithium and diethylcadmium, were analyzed for lithium by acidimetric titration with a pH-meter, and for zinc and cadmium by complexometric titration using ethylenediamine tetraacetic acid in the presence of Eriochrome Black T.

NMR measurements

The spectra were obtained with a Varian A-60 spectrometer (36°). The Pyrex sample tubes for NMR spectra were provided with a rubber cap and filled under argon with a gas-tight syringe. The concentration of the solution was of the order, 10^{-1}–$5 \cdot 10^{-1}$ *M*.

The solvent (benzene) was used as internal reference.

The relative concentrations of ethers and organometallic compounds were deduced from the integrated areas of their resonance signals with an accuracy of 3–6%. The chemical shifts were measured with a precision of 0.2%.

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SUMMARY

NMR spectroscopy was used for investigating the formation of *ate* complexes between ethyllithium and the ethyl compounds of three metals of Group IIB. The changes of the methylic triplet and methylenic quadruplet were followed as a function of the initial ratio of the two reagents in the solution.

It was observed that: (a) ethyllithium and diethylmercury in benzene exchange their ethyl groups very slowly; (b) a fast exchange reaction takes place between ethyllithium and diethylcadmium in benzene, without however, formation of any detectable

ate complex; on the addition of a small amount of diethylether (Et_2O) or tetrahydrofuran (THF), a 1 : 1 complex, lithium triethylcadmium, is formed which is more stable in the presence of the cyclic ether; (c) a 1.1 complex, $(C_2H_5)_3ZnLi$, is formed in pure benzene as well as in a mixed reaction medium: benzene + diethylether or benzene + THF.

On the addition of various amounts of ether to a lithiumtriethylzinc solution in benzene, the changes of the ethyl signals demonstrate the existence of the following species: $LiEt_3Zn \cdot Et_2O$, $LiEt_3Zn \cdot (THF)_2$, $LiEt_3Zn \cdot DME$. Similarly, the formation of $LiEt_3Cd(THF)_2$ by the addition of THF to a benzene solution of EtLi and Et_2Cd has been investigated.

REFERENCES

1 J. Furukawa, *Polymer*, 3 (1962) 487.
2 T. Tsuruta, T. Makimoto and Y. Nakayama, *Makromol. Chem.*, 90 (1966) 12.
3 G. L'Abbé and G. Smets, *J. Polymer. Sci.*, in press.
4 J. Vandendael, *Ph. D. Thesis*, Louvain, October, 1966.
5 J. Debras, *Licence-Thesis*, Louvain, 1966.
6 W. Tochtermann, *Angew. Chem.*, 5 (1966) 531.
7 D. T. Hurd, *J. Org. Chem.*, 13 (1948) 711.
8 L. M. Seitz and T. L. Brown, *J Am. Chem. Soc.*, 88 (1966) 4140.
9 T. L. Brown, D. Dickerhoff and D. Bafus, *J. Am. Chem. Soc.*, 84 (1962) 1371.
10 D. F. Evans and J. P. Maker, *J. Chem. Soc.*, (1962) 5125.
11 P. T. Narashiman and M. T. Rogers, *J. Am. Chem. Soc.*, 82 (1960) 34.
12 H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 25 (1956) 1228.
13 G. Wittig, F. J. Meyer and G. Lange, *Ann.*, 571 (1951) 167.
14 F. Hein and H. Schramm, *Z. Physik. Chem.*, A151 (1930) 234.
15 K. H. Thiele and S. Schröder, *Z. Anorg. Allgem. Chem.*, 337 (1965) 14.
16 Z. K. Cheema, G. W. Gibson and J. F. Eastham, *J. Am. Chem. Soc.*, 85 (1963) 3517.
17 R. Schlenck and J. Holtz, *Ber.*, 50 (1917) 272.
18 C. Noller, *Org. Syn.*, Vol. II, p. 184.
19 R. Schlank and H. Schechter, *J. Org. Chem.*, 24 (1959) 1825.