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Preliminary communication

THE DIRECT SYNTHESIS OF POLY(*N*-ALKYLIMINOALANES)

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Summary

A novel direct synthesis of poly(*N*-alkyliminoalanes) is described; it involves treatment of aluminum metal with primary amines in hydrocarbon solvents under a pressure of hydrogen.

Much work has been carried out in our laboratories on the syntheses and characterization of alane derivatives and especially of poly(*N*-alkyliminoalanes) (PIA) [1-5], which can behave relevant as polymerization catalysts [1] and reducing agents [6]. In previous papers, we examined many routes for the synthesis of PIA and showed how the structure of PIA depends on the nature of the amine and on the experimental conditions and how, in turn, the structural variations markedly influence catalytic activity in polymerization. More recently, we described a simpler method [7], which gives PIA in quantitative yield according to eqn. 1.

$$MAlH_4 + RNH_2 \xrightarrow{\text{hydrocarbon}} \frac{1}{n}(HAlNR)_n + 2H_2 + MH \qquad (1)$$

M = Na, Li

Starting from t-$C_4H_9NH_2$ or primary amines having a nitrogen with α- or β-secondary carbon atoms, well defined PIA tetramers and/or hexamers are obtained. From linear amines or when employing polar solvents, complexes of PIA with MH are formed, which in some cases are completely insoluble. The combination of reaction 1 with the well known reaction 2 [8], which regenerates $MAlH_4$

$$MH + Al + 3/2\,H_2 \rightarrow MAlH_4 \qquad (2)$$

corresponds to eqn. 3.

$$Al + RNH_2 \rightarrow \frac{1}{n}(HAlNR)_n + \tfrac{1}{2}H_2 \qquad (3)$$

TABLE 1

RESULTS OBTAINED IN THE DIRECT SYNTHESIS OF POLY(*N*-ALKYLIMINOALANES)[a] (PIA)

Example	Amine (mmol)	Activator (mmol)	Atomic ratio N/Al in soln.	PIA yield (%)	Analysis Found (*Calcd*)[b] Al (%)	N (%)	H_{act} (meq/g)	ν(Al—H)[c] (cm^{-1})	Mass spectrometry and ^1H NMR[d]
1	i-$C_3H_7NH_2$ (180)	$NaAlH_4$ (9.4)	0.08	100	29.85 (31.71)	16.35 (16.46)	11.31 (11.75)	1850	hexamer
2	i-$C_3H_7NH_2$ (180)	$(HAlN\text{-}i\text{-}C_3H_7)_6$ (1.75)	1.12	⩾ 85	31.05 (31.71)	16.60 (16.46)	9.95 (11.75)	1850	prevailingly hexamer
3	n-$C_3H_7NH_2$ (207)	$NaAlH_4$ (9.0)	1.04	100	29.55 (31.77)	15.92 (16.46)	10.75 (11.75)	1815, 1855	octamer
4	t-$C_4H_9NH_2$ (190)	$NaAlH_4$ (9.3)	1.5[c]	ca. 25	27.01 (27.22)	15.10 (14.13)	9.71 (10.09)	1850	tetramer

[a] Commercial aluminum (99.5%) was deoxygenated by milling with 2% mole of $AlEt_3$ in toluene (examples 1, 3 and 4) or with 1% of $(HAlN\text{-}i\text{-}C_3H_7)_6$ (example 2). Before use, the $AlEt_3$ was removed by filtration and then washing of the milled aluminum several times with toluene.
Reaction conditions: toluene 280 ml; Al 200 mmoles, H_2 200 kg/cm^2, 180°C, 16 h (n-heptane can be used with similar results). [b] Denotes that the solid examined was obtained by evaporation of the reaction solution in order to give quantitative yields; in other cases the solid was examined after recrystallization. [c] In Nujol mull. [d] See ref. 3. [c] Mass spectrometry shows the formation of different imino derivatives [$(M - CH_3)^+$ at m/e 572, 501, 456, 430] besides tetra(*N*-t-butyliminoalane).

We have now succeeded [9] in carrying out this direct synthesis of PIA in a ne step process, using a small amount of $MAlH_4$ as an activator. The reaction ocurs in both aliphatic and aromatic hydrocarbon solvents at fairly high temperaures under hydrogen pressure, and gives quantitatively yields of pure and well deined PIA oligomers even from primary amines, which give insoluble products or mixture of oligomers by other methods. Several promotors are found to speed p reaction 3, the simplest being PIA itself. In Table 1 the results of some prelimnary tests are listed.

For applications which need the absolute absence of polar solvents, e.g. olymerization processes, the advantage of obtaining hydrocarbon solutions of ctive PIA in one step is of paramount importance.

Research in progress is directed at establishing the influence of the nature of the amine and the reaction conditions on the structure of the PIA obtained.

References

1 A. Mazzei, S. Cucinella and W. Marconi, Makromol. Chem., 122 (1969) 168.
2 A. Mazzei, W. Marconi and A. Baradel, Chim. Ind. (Milan), 51 (1969) 447; Ital Pat. 1965, 732905.
3 S. Cucinella, T. Salvatori, C. Busetto, G. Perego and A. Mazzei, J. Organometal. Chem., 78 (1974) 185.
4 M. Cesari, G. Perego, G. Del Piero, S. Cucinella and E. Cernia, J. Organometal. Chem., 78 (1974) 203.
5 Ital. Pat. Appl. 24661 A/74, 24662 A/74 and 24663 A/74 (SNAM Progetti).
6 G.M. Giongo, F. Di Gregorio, N. Palladino and W. Marconi, Tetrahedron Lett., (1973) 3195.
7 Ital. Pat. Appl. 31857 A/73 (SNAM Progetti).
8 E.C. Ashby, G.J. Brendel and H.E. Redman, Inorg. Chem., 2 (1963) 499.
9 Ital. Pat. Appl. 25941 A/74 (SNAM Progetti).