New Class of Polymers containing Tin–Neocarborane Sequences

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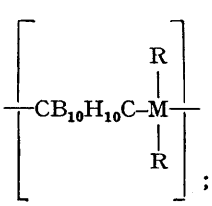
THE synthesis of organometallic polymers containing Group IVB elements has received considerable attention; linear polymers with the metal in the main chain can be obtained by poly-addition reactions involving organometallic dihydrides and diolefinic compounds.[1]

Our interest is in the synthesis of new polymers formed from dilithium–neocarborane and dialkyl- or diaryl-metal dihalides (the metal being a Group IVB element), in which the structural unit is represented by



in particular the conditions under which diphenylstanno–neocarborane polymers can be synthesized.

Dilithium-neocarborane and diphenyltin dichloride in the molar ratio 1:1 were allowed to react in tetrahydrofuran. The influence of temperature, time of reaction, and reagent concentrations have been examined. The results obtained are listed; the number-average molecular weights were determined by the Mechrolab Osmometer type 301A, in tetrahydrofuran solution.

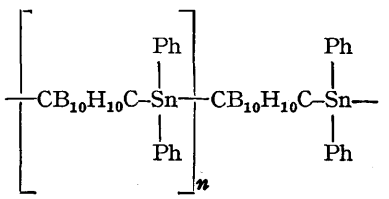
The products are colourless, amorphous substances and, with the exception of product obtained in run 5, readily soluble in tetrahydrofuran, chloroform, sparingly soluble in benzene and insoluble in acetone, alcohols, diethyl ether, and aliphatic hydrocarbons. They are air-stable and no decomposition occurs at the softening points, which are dependent on the degree of polymerization. As an example, the product obtained in run 1 was fractionated into four samples and the number-average molecular weights were between 514—5750: the low-molecular-weight fraction has the softening point at about 52° while the 5750-$\overline{M}$ sample shows a softening point at about 260°.

Data in the Table show that the concentration of reagents has a remarkable influence on the molecular weights of the products, whereas temperature and time of reaction appear to be of little effect.

TABLE

Run No.	Concn. Reagents (M × 10)	Temperature (°c)	Time (hr.)	Yield (%)	$\bar{M}$
1	1·44	20	40	83	1370
2	1·44	30	24	88	1010
3	1·44	30	48	90	1010
4	2·88	0	16	42	1830
5	2·88	0	46	53	not soluble
6	2·88	30	16	52	1990
7	2·88	30	40	57	2120
8	2·88	50	16	58	1900
9	2·88	50	40	54	1650

From analytical data and i.r. spectra the following linear structure for the polymers is suggested:



A backbone of tin and neocarborane sequences in linear polymers can be formed starting from neocarborane which, owing to its geometry with the carbon atoms in "*meta*"-positions, is thought to preculde its participation in forming exocyclic rings.[2] When dilithium-neocarborane is replaced by the isomeric dilithium-carborane, the product of this reaction with dialkyltin dichlorides is a cyclic compound containing two tin atoms per molecule.[3]

From these preliminary results, it appears that the synthesis of polymers, consisting of tin and neocarborane sequences, may be carried out successfully. These polymeric substances, in view of the stability of the carbon–tin and the thermal integrity of the neocarborane nucleus at high temperatures, are likely to exhibit interesting physical and chemical properties.

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[2] S. Papetti and T. L. Heying, *Inorg. Chem.*, 1964, **3**, 1448.
[3] L. I. Zakharkin, V. I. Bregadze, and O. Yu. Okhlobystin, *J. Organometallic Chem.*, 1965, **4**, 211.