

BEHAVIOUR OF DICARBA-*closo*-DODECABORANES IN THE POLYMERIZATION OF CAPROLACTAM

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The polymerizations of ϵ -caprolactam, hydrolytic, anionic, and cationic, were carried out with the addition of isomeric dicarba-*closo*-dodecaboranes. While 1,12-dicarba-*closo*-dodecaborane always acts as an inert component, 1,2- and 1,7-dicarba-*closo*-dodecaboranes affect the polymerization and yield degradation products, probably by a reaction with nucleophilic groups present in the mixture. If the polymerization does proceed in presence of the above two isomers, it is possible to assume that their fragments are bonded to the end of the polycaprolactam chain in the form of an ammonium salt.

Inorganic compounds are used in the preparation of polyamides either for direct modification of the chain on the terminal groups or as fillers which influence the structure of the solid polymeric phase, and thus also some properties of the polymer. In recent years, a number of papers have been dealing with the preparation and polymerization of monomers containing carborane structures in their molecule. Koršák and coworkers prepared aromatic polyamides with 1,7- and 1,12-dicarba-*closo*-dodecaborane structures in the diacid¹⁻³ or diamine⁴ chain unit in order to enhance the thermal and radiation stability of these polymers⁵⁻⁷.

We decided to investigate the behaviour of 1,2-, 1,7- and 1,12-dicarba-*closo*-dodecaborane under the polymerization conditions of ϵ -caprolactam because we believed that already the mere addition of carboranes to the polymerizing lactam could lead to the incorporation of the dicarbadodecaborane structure or of its fragment into the resulting polymer, or to physical interactions between carborane and polyamide leading to a modification of the polymer properties. Lactam could also be used as a comonomer with the carborane monomers described earlier¹⁻⁴ in the preparation of polyamides. For this reason, we studied the stability of dicarba-*closo*-dodecaboranes towards the reducing caprolactam medium at high polymerization temperatures in presence of various initiators of polymerization, as well as the effect of carboranes on the polymerizability of caprolactam by various polymerization routes.

EXPERIMENTAL

Chemicals. Purification and drying of ϵ -caprolactam and preparation of sodium caprolactam⁸, N-benzoylcaprolactam⁹ and ϵ -aminocaproic acid have been described earlier. Octadecyl amine

hydrochloride was prepared by introducing a stoichiometric amount of dry hydrogen chloride into a 10% solution of amine in absolute ethanol; it was used after recrystallization from absolute ether and drying *in vacuo* 260 Pa/50°C. 1,2-Dicarba-*closo*-dodecaborane, m.p. 294.5 to 295.5°C, was purified by sublimation and crystallization from hexane; its purity was proved by TLC, GLC, and IR spectroscopy. 1,7-Dicarba-*closo*-dodecaborane was prepared¹⁰ by the thermal isomerization of its 1,2-isomer at 520°C; repeated sublimation yielded a uniform product (TLC, GLC), m.p. 272–3°C. 1,12-Dicarba-*closo*-dodecaborane was prepared¹¹ by the continuous thermal isomerization of its 1,2-isomer in a stream of nitrogen at 720°C, and was uniform after crystallization from hexane and sublimation (TLC, GLC, GPC), m.p. 260–261°C.

The *polymerizations* were carried out in sealed glass ampoules containing 0.8–1.5 g of the polymerization mixture and 0.5–1 ml of vapour space. The ampoules were charged with the separately prepared polymerization mixture in an inert dry atmosphere, as has been described earlier¹². To prepare the polymerization mixtures, initiator and, if needed, activator were dissolved in molten caprolactam at 80–90°C; the respective carborane was dissolved last.

Analysis of the polymerization product. The polymer content in the product of polymerization was determined by extraction with boiling water¹³ and drying of the polymer at 50°C/130 Pa. Viscosity of the extracted polymer was measured in *m*-cresol at 25°C and at a concentration 0.4 g/dl; intrinsic viscosity was calculated from single measurement by means of the Huggins constant 0.4. Free dicarba-*closo*-dodecaboranes were determined in methanolic extracts of the polymers or in polymer solutions in *m*-cresol or trifluoroethanol by gas chromatography under following conditions; stainless-steel columns 1 m × 3 mm packed with 15% of polyethylene glycol adipate on Chromosorb W (80–100 mesh), the column temperature 170°C, nitrogen carrier gas 50 ml/min; Perkin-Elmer F 11 chromatograph with a flame ionization detector and integrator D 26.

Boron concentration in the extracted polymers was determined by the $n - \gamma$ reaction in a nuclear reactor¹⁴. The maximum boron concentration corresponding to one $(B_9C_2H_{12})^{(-)}$ anion in each macromolecule, was calculated from the expression for the number average degree of polymerization $\bar{P}_n = 119[\eta]^{1.34}$. The qualitative test of the presence of the reducing anion $(B_9C_2 \cdot H_{12})^{(-)}$ was performed by a spot method on filtration paper with the trifluoroethanol solution of the extracted polymer and silver nitrate¹⁵.

RESULTS AND DISCUSSION

The polymerization of ϵ -caprolactam in presence of three isomeric dicarba-*closo*-dodecaboranes was carried out with three types of initiators: hydrolytic polymerization initiated with ϵ -aminocaproic acid, activated anionic polymerization initiated with sodium ϵ -caprolactam in presence of N-benzoylcaprolactam as an activator, and cationic polymerization initiated with octadecyl amine hydrochloride.

Hydrolytic Polymerization

The results are summarized in Table I. They depend on the type and concentration of dicarba-*closo*-dodecaborane used, and partly also on the polymerization temperature (230 or 250°C); the polymerization without additive is given for the sake of comparison. 1,12-Dicarba-*closo*-dodecaborane behaves during the polymerization as an inert diluent. The decrease in the polymer yield is in part due to a shift of the

polymer-monomer equilibrium in the presence of diluent¹⁶ (by some 1% at the concentration used) while the degree of polymerization remains practically unchanged. The further part of this decrease is due to volatilization of carborane during extraction with boiling water. Gas chromatography of the methanolic extracts of polymerization products or directly of the product solutions in *m*-cresol revealed an average of 90% of the originally added carborane. The remaining about 10% occurs in the vapour phase above the melt during the polymerization, and condenses on the ampoule walls on cooling.

On the contrary, an addition of 1,7-dicarba-*closo*-dodecaborane considerably reduces the polymer yields, if carborane is present in excess with respect to the initia-

TABLE I

Polymerization of Caprolactam Initiated with ϵ -Aminocaproic Acid

[I] Initial concentration of initiator (mmol/kg), [B] initial concentration of carborane (mmol/kg), *p* polymer yield.

Experiment	[I]	[B]	<i>T</i> , °C	<i>t</i> , h	<i>p</i> , %	$[\eta]$, dl/g
1	870	—	230	25	91.0	0.92
1,2-Dicarba- <i>closo</i> -dodecaborane						
2	645	1 288	230	24	31.9	
3	830	325	230	4	51.0	0.22
4	830	325	230	25	82.6	—
5	830	325	250	3	58.9	—
6 ^a	85	325	250	63	—	—
1,7-Dicarba- <i>closo</i> -dodecaborane						
7	830	325	230	4	62.4	0.27
8 ^b	830	325	230	25	82.8	0.39
9 ^c	85	325	230	50	35.1	0.22
1,12-Dicarba- <i>closo</i> -dodecaborane						
10	830	325	230	4	84.1	0.84
11	830	325	230	25	87.6	0.90
12	85	330	230	50	81.3	1.63
13	830	325	250	3	86.4	0.81
14	830	325	250	13	86.2	0.82
15	85	330	250	50	86.1	1.75

^a Nonhomogeneous orange-coloured polymerizate, gaseous products. ^b After 20 h, separate bubbles are formed in polymer. ^c Degradation of polymer occurred during heating.

tor, and gaseous decomposition products are formed already at 230°C. 1,2-Dicarbap-*closo*-dodecaborane behaves in a similar way. In its presence, gaseous and coloured degradation products are formed only after heating to 250°C for rather a long time. Since the latter carborane was detected by gas chromatography neither in the methanolic extract of the polymerization product nor in the product solution in trifluoroethanol, boron was looked for in polymers extracted with water and methanol.

A number of authors¹⁷⁻²¹ have demonstrated that 1,2- and 1,7-dicarbap-*closo*-dodecaboranes react with nucleophilic agents, such as alkaline alkoxides, amines and ammonia, with elimination of one boron atom adjacent to both carbon atoms from the icosahedral skeleton with formation of 7,8-dicarbap-*nido*-undecaborate anions ($B_9C_2H_{12}$)⁽⁻⁾; simultaneously, elemental hydrogen is formed in this reaction. It may be assumed that the above dicarbap-*closo*-dodecaboranes react similarly with the amino groups of the initiator and polyamide chain in the polymerization mixture. The resulting anions ($B_9C_2H_{12}$)⁽⁻⁾ probably form a comparatively stable ammonium salt with the terminal amino groups of the polymer. In accordance with this view, the amount of boron determined in extracted polymers did not exceed the amount corresponding to one ($B_9C_2H_{12}$)⁽⁻⁾ per polymer chain, as follows from the values of B_p and B_m summarized in Table II. Such an assumption is justified and confirmed by the reduction of silver from its salts with trifluoroethanol solutions of these polymers,

TABLE II

Boron Content in Extracted Polymers

[B]_p determined, [B]_m calculated maximum; ($B_9C_2H_{12}$)⁽⁻⁾ test: - negative, + positive, ++ strongly positive.

Experiment	Carborane ($B_9C_2H_{12}$) ⁽⁻⁾	[B] _p , %	[B] _m , %	
Hydrolytic polymerization				
1	—	—	0	—
2	1,2—	++	5.0	—
3	1,2—	++	4.7	5.5
7	1,7—	+	1.8	4.2
8	1,7—	+	2.4	2.6
10	1,12—	—	—	—
14	1,12—	—	—	—
Cationic polymerization				
50	1,2—	++	2.9	4.4
51	1,7—	++	0.6	4.0
52	1,12—	—	0.1	3.6

which indicates the presence of the strongly reducing $(B_9C_2H_{12})^\ominus$ anions. It was proved that if the polymers were reextracted with water and methanol, the extracts did not reduce Ag^+ . It is known that low-molecular weight ammonium and cesium salts of the above anions are also stable and can be crystallized from water.

The reaction of carborane with forming amino groups can also be employed to explain why Koršak and coworkers⁵ have always found, during the thermal degradation of polyamides containing 1,7-dicarba-*closo*-dodecaborane structure units in their chain, elemental hydrogen as the first and main gaseous product, even at temperatures starting from 200°C when the thermal splitting of polymer chains has not yet set in. On the other hand, 1,12-dicarba-*closo*-dodecaborane skeleton is rather inert to nucleophilic agents even at elevated temperatures, which is also corroborated by our results.

Anionic Polymerization

A similar interpretation can be used for the results obtained in the activated anionic polymerization of caprolactam in presence of carboranes (Table III). The negative effect of 1,2- and 1,7-dicarba-*closo*-dodecaboranes on the course of polymerization could be observed even at a lower temperature and a shorter polymerization time, because the process involved in this case is not the thermal destruction of the additive but the reaction with a nucleophilic agent discussed above. Since the anionic polymerization of lactams depends on the presence of lactam anions which in this case are quantitatively consumed by the carboranes present in the mixture, the polymerization could not take place. The chromatographically determined residue of 1,2-dicarba-*closo*-dodecaborane roughly corresponds to the initial amount minus a portion equivalent to the initiator used. For higher concentrations of carborane, the decrease in concentration is lower and lies within the limits or error of the analytical method. The formation of gaseous products (obviously hydrogen) can be observed already during the preparation of the polymerization mixture, *i.e.* during the dissolution of 1,2- and 1,7-isomers in the caprolactam solution of sodium caprolactam at 80–90°C. In the case of 1,7-dicarba-*closo*-dodecaborane under the conditions of anionic polymerization, there probably occurs a deeper decomposition with release of a large amount of gaseous products (hydrogen) which causes explosions of the polymerization ampoules. Only 1,12-dicarba-*closo*-dodecaborane again acts as an inert diluent and reduces the equilibrium content of the polymer and the rate of establishment of the polymerization equilibrium proportionately to the amount added, as follows from the comparison of experiments 16–21 and 35–46 (Table III). In this case again, no effect of the additive on the viscosity of the polymer could be observed. One part of the increased portion of the extract again consists of carborane which has evaporated during the extraction at the higher temperature. A homogeneous polymer with dissolved carborane is formed in a concentration range of the added

TABLE III

Anionic Polymerization of Caprolactam Initiated with Sodium ϵ -Caprolactam and Activated with N-Benzoylcaprolactam

Initial concentration of components (mmol/kg): [I] initiator, [A] activator, [B] carborane, p polymer yield, $[B]_f$ carborane content in the polymerization product (related to [B]).

Experi- ment	[I]	[A]	[B]	$T, ^\circ\text{C}$	t, h	$p, \%$	$[B]_f, \%$	$[\eta], \text{dl/g}$
16	26	26	—	190	0.30	93.8	—	3.26
17	26	26	—	190	1	97.1	—	3.12
18	26	26	—	190	4	97.5	—	2.82
19	26	26	—	230	0.25	90.9	—	2.83
20	26	26	—	230	1	90.8	—	2.37
21	26	26	—	230	4	90.8	—	1.98
1,2-Dicarba- <i>closo</i> -dodecaborane								
22	26	26	68	190	0.33	0	59	—
23	26	26	68	190	1	0	47	—
24	26	26	68	190	4	0	45	—
25	25	25	327	190	0.33	0	100	—
26	25	25	327	190	1	0	100	—
27	25	25	327	190	4	0	100	—
28	26	26	68	230	0.25	0	—	—
29	26	26	68	230	1	0	41	—
30	26	26	68	230	4	0	24	—
31	25	25	327	230	0.25	0	100	—
32	25	25	327	230	1	0	92	—
33	25	25	327	230	4	0	95	—
1,7-Dicarba- <i>closo</i> -dodecaborane								
34 ^a	40	20	625	175	16	0	—	—
1,12-Dicarba- <i>closo</i> -dodecaborane								
35	26	26	68	190	0.30	91.9	—	2.80
36	26	26	68	190	1	95.9	—	2.88
37	26	26	68	190	4	96.9	—	2.86
38	25	25	327	190	0.30	89.4	—	3.05
39	25	25	327	190	1	92.3	—	3.29
40	25	25	327	190	4	94.5	—	2.95
41	26	26	68	230	0.25	90.6	—	2.63
42	26	26	68	230	1	90.4	—	2.49
43	26	26	68	230	4	90.3	—	2.02
44	25	25	327	230	0.25	88.3	—	2.71
45	25	25	327	230	1	88.4	—	2.53
46	25	25	327	230	4	88.1	—	1.98
47	25	25	327	250	4	86.9	—	1.27
48 ^b	40	20	520	175	1	76.5	—	—

^a Gaseous products. ^b Heterogeneous polymerization mixture and product.

1,12-isomer up to 5 wt. % (330 mmol/kg) per caprolactam used. At higher concentrations (*cf.* experiment 48) both the initial polymerization mixture and the polymer formed are already heterogeneous.

Cationic Polymerization

Preliminary results of polymerization (Table IV) can also be explained on the basis of the above behaviour of dicarba-*closo*-dodecaboranes. It is known that the polymerization of caprolactam with amine hydrochlorides as initiators slows down even before reaching the monomer-polymer equilibrium²² after the initial fast period. At the same time, the concentration of initiator decreases and basic groups arise in the polymerization system, probably the amine and amidine ones²³. This is also corroborated by the polymer yields in experiments 49–52 (Table IV), as well as by the formation of gaseous products in presence of 1,2- and 1,7-dicarba-*closo*-dodecaboranes in later stages of the polymerization. The formation of gases – apparently, hydrogen – again takes place in that stage of polymerization for which one may already assume the interaction of carborane with basic groups; the polymer yield is lower than for the reference experiment 49 and for the polymerization involving the 1,12-isomer. These polymers show also the $(B_9C_2H_{12})^{(-)}$ test and the amount of bonded boron in accordance with the above assumption about the ionic bond on the basic terminal groups. At the same time, 0.1 wt.% B in the polymer prepared with the 1,12-isomer is a measure of the boron amount which can be retained by the extracted polymer in a way different from the chemical bond, *e.g.* by sorption.

Generally, 1,12-dicarba-*closo*-dodecaborane added to the polymerization mixture can be characterized as an inert compound which remains stable at temperatures up to 250°C. Under these conditions, 1,2- and 1,7-dicarba-*closo*-dodecaboranes undergo degradation probably by an interaction with the nucleophilic groups (amide anions, amines, amidines) forming hydrogen and the $(B_9C_2H_{12})^{(-)}$ anions. At the

TABLE IV
Cationic Polymerization of Caprolactam Initiated with Octadecyl Amine Hydrochloride (325 mmol/kg) in Presence of Carboranes (325 mmol/kg) at 230°C (polymer yield, *p*, after 20 h).

Experiment	Carborane	<i>p</i> , %	$[\eta]$, dl/g
49	—	81.5	0.30
50	1,2-dicarba- <i>closo</i> -dodecaborane	68.6 ^a	0.26
51	1,7-dicarba- <i>closo</i> -dodecaborane	68.4 ^a	0.28
52	1,12-dicarba- <i>closo</i> -dodecaborane	79.5	0.30

^a Foam is formed on the polymerizate surface.

same time, these isomers seem to influence the polymerization more or less depending on the chosen initiation system and their fragments are probably bonded by ionic bonds to the terminal basic groups of the forming polymer.

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