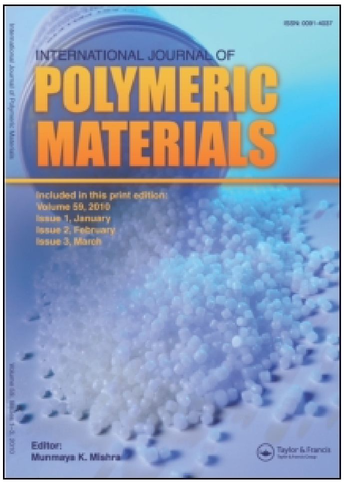

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Rusanov, A. , Komarova, L. , Kats, G. and Prigozhina, M.(1994) '*m*-Carborane-containing Polyamides as Stabilizers for Polyheteroarylenes', International Journal of Polymeric Materials, 25: 1, 117 — 122
To link to this Article: DOI: 10.1080/00914039408028583
URL: http://dx.doi.org/10.1080/00914039408028583

Intern. J. Polymeric Mater., 1994, Vol. 25, pp. 117–122
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Printed in Malaysia

m-Carborane-containing Polyamides as Stabilizers for Polyheteroarylenes

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The potential of *m*-carborane-containing polyamides as stabilizers for polyheteroarylenes is discussed.

KEY WORDS Stabilization, carboranes, polyamides, heterocyclic polymers

RESULTS AND DISCUSSION

The idea of utilizing (carborane-containing polyamides for the stabilization of some polymers is based on the nature of carboranes, e.g., the ability of the *o*- and *m*-isomers to degrade with the formation of dicarbanido-undecaborane anion[1]:

$$RCB_{10}H_{10}CR + CH_3O^- + CH_3OH \xrightarrow[40°C]{KOH} RCB_9H_{10}CR^- + B(OCH_3)_3 + H_2$$

The degradation process proceeds easily for the carborane amino-derivatives, especially for the compounds where the amine nitrogens are directly adjacent to the carborane cage's carbon atoms. This is why polyamides based on *m*-carboranedicarboxylic acid $—[OCCB_{10}H_{10}CCO—HNC_6H_4NH—]_n$ and *m*-carboranylenediamine $—[OCC_6H_4CO\text{-}HNCB_{10}H_{10}CNH—]_n$, are effective thermostabilizers for different classes of polymers.[2]

Spectral investigations of the polyamides based on *m*-carboranedicarboxylic acid showed that dicarbanide-undecaborate groupings were formed in sufficient quantities at 300°C. At the same temperature these same polyamides demonstrate the stabilizing activity under conditions of heating both *in vacuo* and in air. As a result the stabilized polymers demonstrate decreased weight loss during high temperature aging and improved mechanical properties. Even low amounts of the *m*-carborane-containing polyamide (0.5–1.0 weight %) are enough to achieve this effect.[3]

Table I presents the results of thermal aging at 400°C in air for the aromatic polyamide obtained by the interaction of terephthaloyl chloride and anilinofluorene (PA)

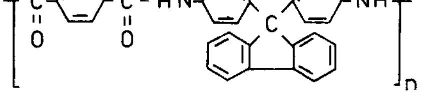


TABLE I

Weight losses (%) of the composition PA-PAC at 400°C in air

	Aging time, hrs			
Sample	1	3	5	8
PA	6.8	19.4	32.2	58.9
PA-PAC	4.1	9.5	12.7	27.4

TABLE II

Some mechanical properties of the shaped articles, obtained by pressing of PA and PA-PAC

Sample	Compressive strength, σ comp., kN/m^2 (kg/cm^2)	Impact strength, kJ/m^2 (kg·cm/cm^2)
PA	10–13 (1000–1300)	1.0 (1.0)
PA-PAC	18–20 (1800–2000)	3.0 (3.0)

and the composition of PA and 0.5 weight % of the poly(*p*-phenylene-*m*-carboranyleneamide) (PAC)

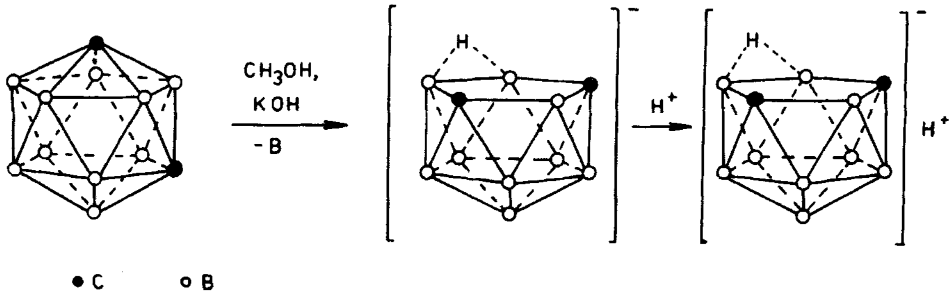
$$\text{—[OCCB}_{10}\text{H}_{10}\text{CCO—HNC}_6\text{H}_4\text{NH]}_n\text{—}$$

Investigation of the thermooxidative degradation of the PA and PA-PAC samples, produced by pressing at 375°C, demonstrated that PAC acts as a PA stabilizer under high temperature conditions. As a result, shaped articles demonstrating improved thermooxidative stability and good mechanical properties were obtained (Table II).

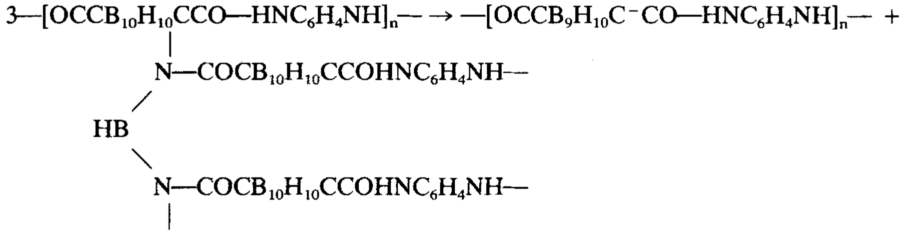
The shaped articles obtained on the basis of unstabilized PA are black and very brittle; on the other hand the shaped articles based on the PA-PAC are strong, monolithic, and light-brown in color.

We suggest that the stabilizing action of the PAC is due to the relatively facile degradation of the *m*-carborane unit.

It is known,[1] that the interaction of *m*-carborane with nucleophylic reagents leads to the loss of a boron atom from the carborane icosaedre and to the formation of the carbonamido structure in accordance with the following scheme:



The reactive boron atom forms—depending on the medium—B—N or B—O links in accordance with the following scheme:



Obviously, dicarbanido-undecaborate fragments formation in PAC is followed with the cross-linking processes. In PA-PAC compositions at high temperatures the chemical interaction between PA and PAC take place, leading to the formation of cross-linked structures, containing strong B—C, B—N and B—O links and possessing enhanced thermal stability. In fact, during the thermooxidation of PA-PAC at 375°C gel-fraction formation takes place almost immediately (Figure 1).

The carbanido-structure of the dicarbanido-undecaborane anion contains an extra-hydrogen; protonation of the anion leads to the formation of the corresponding acid. This additional proton is called, in the carborane chemistry, "extra-extra" hydrogen. Due to the electron-withdrawing properties of the *m*-carborane amide protons, *m*-carborane containing polyamides are rather acidic; as a result the process of anion protonation at elevated temperatures may proceed easily.

The formation of the dicarbanido-undecaborane anion and its properties were studied for the example of *m*-carboranedicarboxylic acid dianilide

$$\mathrm{Ph{-}NH{-}CO{-}CB_{10}H_{10}C{-}CO{-}HN{-}Ph}$$

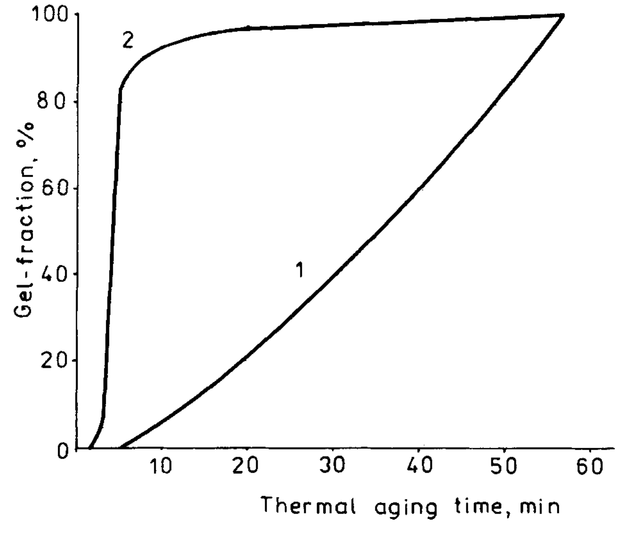


FIGURE 1 Kinetic curves for gel-fraction formation for PA (1) and PA-PAC (2) thermal aging at 375°C.

which may be considered as a model compound for *m*-carboranecontaining polyamide.[4] It was found, that in the protonated state the $[\mathrm{Ph{-}NH{-}CO{-}CB_9H_{10}C{-}CO{-}HN{-}Ph}]^-\mathrm{H}^+$ "extra-extra" hydrogen interacts with $\mathrm{{-}CO{-}CH_9H_{10}C{-}CO^-{-}}$ fragment destabilizing the carbanido-icosaedre, with its subsequent degradation and formation of acetanilide and a residue containing products of deep degradation of carbanido-carborane, e.g., under the action of atmospheric oxygen and moisture the C—B links of the dicarbanido-undecaborate fragments degrade and the carbon atoms combine with the organic portion of the molecule. In polymers this process leads to the degradation of the carborane C—B links in the macromolecules. Residues of the macromolecules contain acetamide and groups, and the reactive boron derivatives participate in the crosslinking process of the stabilized polymer forming very stable B—C, B—N and B—O links.

Carbanido-polyhedre degradation is not only the first step in the formation of carbanido structure, but it is followed by hydrogen elimination.[5] The amount of hydrogen eliminated exceeds the amount of other volatile degradation products: CO, CO_2, H_2O, and CH_4. Differential curves of gas evolution during PAC pyrolysis are given in Figure 2.

We believe, that evolution of the first hydrogen portion is connected with degradation of the *m*-carborane cage in the polyamide and formation of dicarbanido-undecaborate anion, as well as with the homolytic scission of the carborane and dicarbanido-undecaborane anion B—H links. Carboranyl radicals formed at the boron atoms transform into stable products via a recombination reaction. These processes also lead to the formation of B—B and B—C links.

It may be suggested that *m*-carborane containing polyamides, undergoing transformations of the *m*-carborane cages containing labile hydrogen atoms, inhibit the radical processes of stabilized polymer degradation. The stabilization principle is similar to the action of such well-known stabilizers as phenols, amines, etc., how-

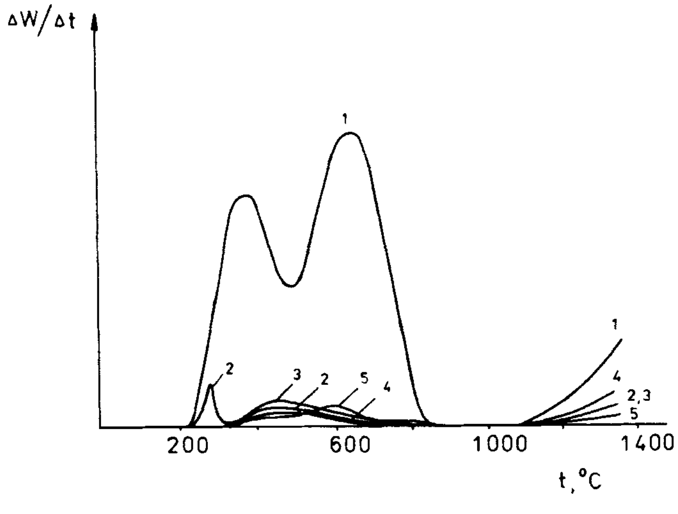
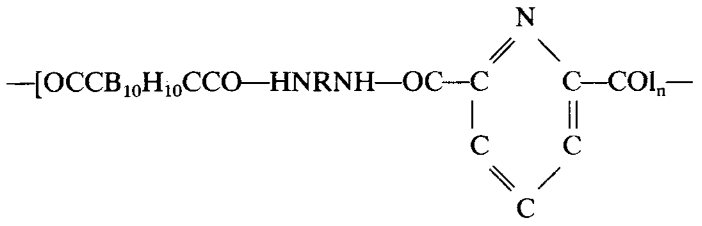


FIGURE 2 Differential curves for gas-evolution during *m*-carborane-containing polyamide pyrolysis: 1-H_2, 2-CO_2, 3-CO_2, 4-H_2O, 5-CH_4. Heating rate 8°/min.

ever, in this case the character of the process is more complicated because of the unusual nature of the stabilizer: the stabilizing action is due not to the anion itself, but to its transformation products, promoting formation of thermally stable bonds. *m*-Carborane-containing polyamide itself acts as a stabilizer, in which the active forms of thermal degradation inhibitor, dicarbanido-undecaborane, is released under the conditions of thermal treatment; as a result it is especially effective at high temperatures.

m-Carborane containing polyamides may be used for the stabilization of polymers degrading at lower temperatures; in these cases it is necessary to decrease the formation temperature of the undecaborate. For this purpose an additional nucleophilic center, pyridine-2,6-dicarboxylic acid residue, was introduced into the polymer backbone.

In copolyamide



m-carborane cleavage followed by formation of dicarbanido-undecaborane anion takes place at ~150°C. This copolyamide is an effective stabilizer for cellulose diacetate. The amount of the carbon oxides, formed during thermal oxidation (250°C, 1 hr) of the cellulose diacetate stabilized with copolyamide decreased 2.5 fold, when compared with an unstabilized sample. The intrinsic viscosity of a stabilized cellulose diacetate solution decreased less than 2 fold compared to a 4 for decrease for the unstabilized cellulose diacetate.

A similar effect may be obtained using polyamide based on 1,7-*m*-carboranylenediamine and terephthalic acid dichloride:

$$—[HN—CB_{10}H_{10}C—NH—OC—C_6H_4—CO]_n—$$

In this polymer dicarbanido-undecaborate "precursors" are formed during the polycondensation reaction[6]; their "liberation" takes place at lower temperatures than for *m*-carboranylendicarboxylic acid based polyamide (150°C).

The addition of such a polyamide to cellulose diacetate leads to a 1.5 fold decrease in weight loss under degradation conditions (*in vacuo*, 1 hr., 250–300°C) compared to unstabilized cellulose acetate. The intrinsic viscosity of solutions of the stabilized compositions are reduced 1.5 fold after 1 hr of heating at 210°C. Under the same conditions the viscosities of such solutions of stabilized polymer decrease 4 times. The amount of stabilizer added doesn't exceed 1–2%.

Even more important may be polymers based on carbanido-carboranes. In these polymers the active thermal aging inhibitor is present in the polymer's structure and it is not necessary to liberate it under conditions of thermal treatment.

The addition of 15 of the polyamide

$$—[OCCB_9H_{10}CCO—HNC_6H_4NH]_n^-—H^+$$

to an aromatic polyamide PA leads to a decrease in the amount of carbon oxides in the degradation products (0.4 mol/mol unit, at 400°C when compared with 0.73 mol/mol unit for unstabilized sample.[7]

m-Carborane-containing polyamides were used successfully for the stabilization of various heterochain and heterocyclic polymers including polyimides and polyphenylquinoxalines.

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