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Synthesis and Properties of Copolymers Having Polyconjugated Blocks in the Macromolecules. IV. Use of Aromatic N,N'-Bis(nitrosoacetyl)diamines for the Synthesis of Carborane-Containing Polymers

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Synthesis and Properties of Copolymers Having Polyconjugated Blocks in the Macromolecules. IV. Use of Aromatic N,N'-Bis(nitrosoacetyl)diamines for the Synthesis of Carborane-Containing Polymers

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ABSTRACT

N-Nitrosoacetylaminophenyl-o-carboranes have been used for the synthesis of polyconjugated polyazophenylene and styrene copolymers containing carborane units. In the presence of carborane-containing polymers, destruction of thermostable polymers in air at high temperatures becomes thermal destruction due to processes of nonchain inhibition.

The high thermostability of polyconjugated compounds (PCC) [1] and the ability of carborane-containing compounds to participate in irreversible binding of oxygen [2] makes promising the creation of new types of thermostable polymers consisting of PCC blocks and

*This paper is dedicated to the memory of A. A. Berlin.

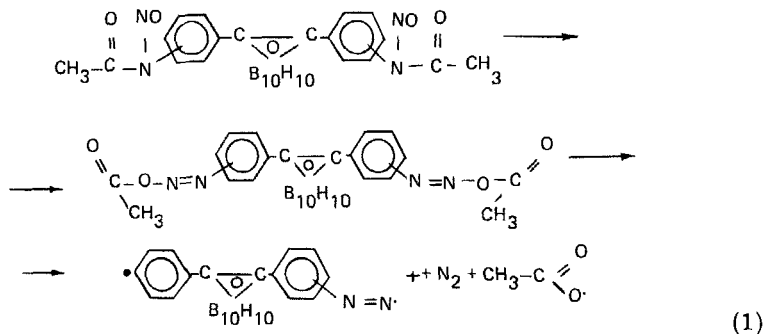
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carborane units. On the other hand, the introduction of carborane units into the molecules of PCC must improve the solubility of the latter.

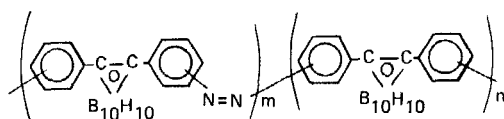
For this reason we studied the possibility of using aromatic N,N' -bis(nitrosoacetyl)diamines for the synthesis of carborane-containing polymers.

SYNTHESIS AND PROPERTIES OF POLYAZOPHENYLENE-O-CARBORANE

The initial substance for the synthesis of polyazophenylene-o-carborane (PAFC) was 1,2-bis(N -nitrosoacetylaminophenyl)-o-carborane (NAFC) obtained by the usual method [3, 4] from 1,2-bis(acetylaminophenyl)-o-carborane. The latter was synthesized from diphenyl-o-carborane by means of nitration, reduction and acetylation under the same conditions as in the case of monoaminophenyl-o-carborane [5]. Like other aromatic nitrosoacetylaminos investigated earlier [6, 7], NAFC decomposes in the solution according to the scheme shown in Eq. (1).



Recombination of phenylene and azophenylene radicals leads to the formation of PAFC.



PAFC

TABLE 1. Kinetics of NAFC Decomposition in Benzene Solution

	$K \times 10^5 \text{ (sec}^{-1}\text{)}$				E (kJ/mole)
	30°C	40°C	45°C	50°C	
NAFC	9.8	28.3	42.6	99.0	84.1
NAB ^a	17.3	46.0	83.3	-	80.7

^aNAB = N,N'-bis(nitrosoacetyl)benzidine.

The kinetics of NAFC decomposition in benzene solution have been studied previously: the decomposition rate was followed by the volume of gaseous nitrogen evolved. The results (Table 1) showed that decomposition rates of NAFC are close to those of earlier studied [7] aromatic nitrosoacetylaminines.

PAFC was obtained in suspension of cyclohexane in water (phase ratio 1:2) at 50°C and at a NAFC concentration in cyclohexane of 7.5 g/liter. The end of polymerization was taken as the cessation of gaseous nitrogen evolution; according to Fig. 1, the polymerization time is equal to 4 hr. Both incomplete nitrogen evolution (36% of theoretical value) and considerable nitrogen content in the polymer (7.46%) are evidence of the participation of azo radicals in the polyrecombination process. The polymer obtained was a light brown powder; the yield was close to 100%. The polymer has a good solubility in chloroform, benzene, dimethylformamide, tetrahydrofuran, and partially dissolves in methanol and acetone.

In the IR spectrum of the polymer (Fig. 2) there are absorption bands of benzene rings and a band at 2600 cm^{-1} which is characteristic of carboranes ($\nu_{\text{B-H}}$). The presence of bands at 1680 and 1375 cm^{-1} indicates the presence of terminal acetoxy groups. The absorption bands at 690 and 735 cm^{-1} , 790 and 690 cm^{-1} , and 850 cm^{-1} correspond to mono-, m-, and p-substituted benzene rings, respectively.

In the electron absorption spectrum of polymer there are maxima at 317 and 328 nm. The absorption in the long-wave region of electron spectrum and high content of paramagnetic centers in the polymer (3.3×10^{17} spins/g according to ESR data) indicate the presence of a conjugated bonds system in the synthesized PAFC.

A low molecular weight fraction was extracted from the polymer by methanol ($\sim 30\%$, $\bar{M}_n = 820$); the higher molecular weight fraction has $\bar{M}_n = 1560$.

From elemental analysis data the ratio m:n in PAFC is equal to 6:1.

PAFC has a high thermal and thermooxidative stability. On heating in helium at 400°C, weight loss does not exceed 9% after 3 hr; in

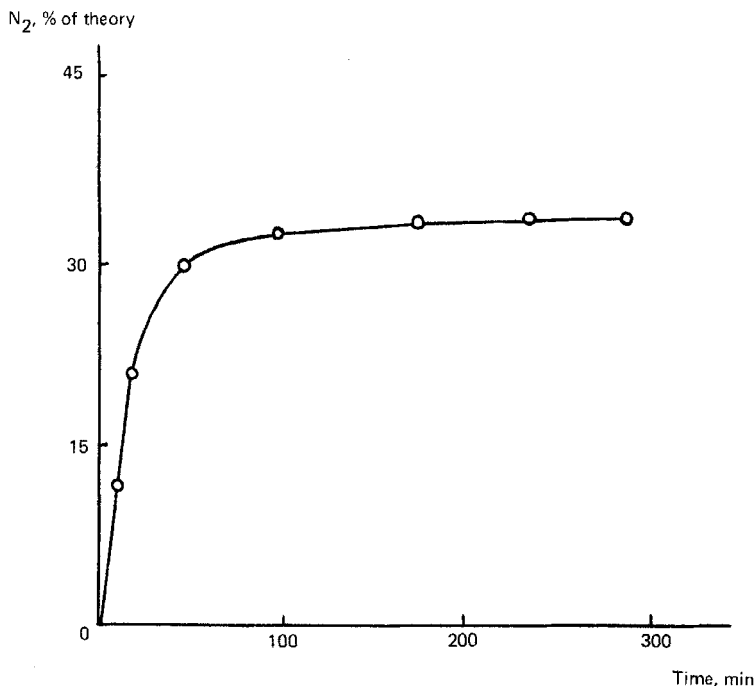


FIG. 1. Evolution of gaseous nitrogen on PAFC formation. Temperature 50°C.

the air, a weight increase is observed (Fig. 3). Earlier [2, 8] the weight increase of carborane-containing compounds at temperatures of 350-450°C was shown to be caused by oxygen addition with the formation of B-O-B bonds accompanied by the appearance of a wide band in the region 1300-1500 cm^{-1} ($\nu_{\text{B-O}}$) in the IR spectra. Apparently in the case of PAFC the same phenomenon takes place, this conclusion being confirmed by the IR spectra (Fig. 2) and DTA (Fig. 4) data. An exothermic peak in the DTA curve caused by the oxidation of B-H bonds and formation of B-O-B bonds corresponds to the beginning of the weight increase in the air.

The ability of PAFC carborane units to add oxygen at high temperatures with the formation of inactive products is of significant interest for the exploitation of the elevation of temperature limit of polyarylenes and can be used for the inhibition of thermooxidative destruction of thermostable polymers.

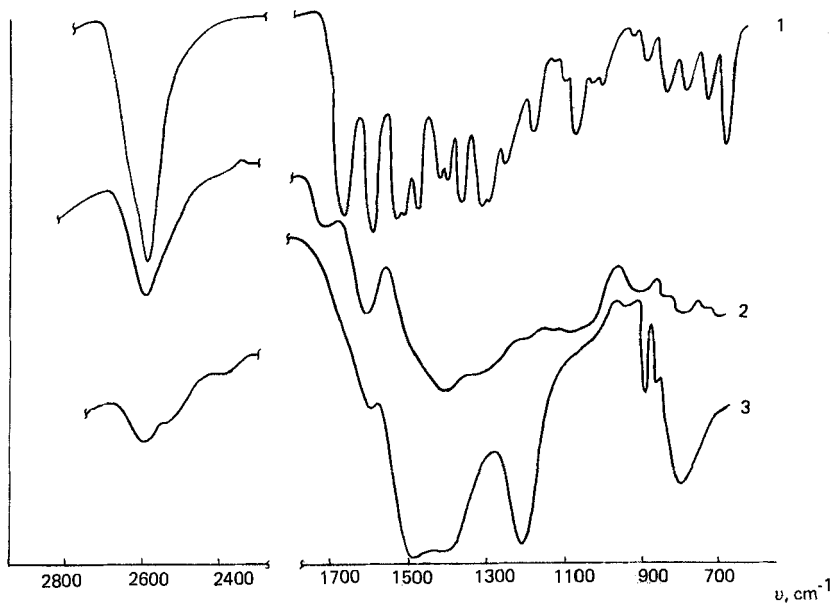


FIG. 2. IR spectra: (1) PAFC; (2) PAFC after heating for 6 hr at 400°C in helium; (3) PAFC after heating for 6 hr at 400°C in air.

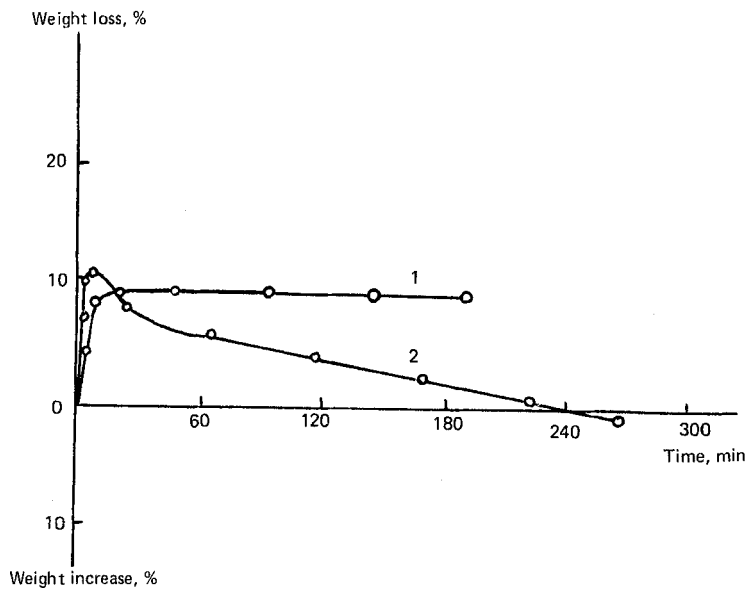


FIG. 3. Isothermic thermogravimetric analysis of PAFC at 400°C: (1) in helium; (2) in air.

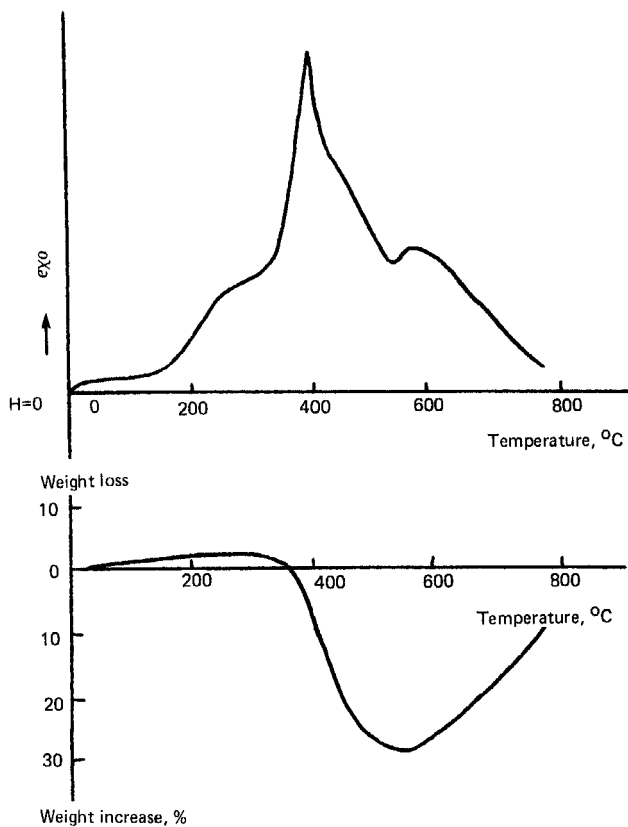


FIG. 4. Dynamic thermogravimetric analysis of PAFC in air. Heating rate, $4.5^{\circ}\text{C}/\text{min}$.

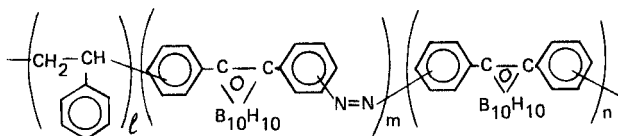
SYNTHESIS AND PROPERTIES OF POLYSTYRENE AND PAFC COPOLYMERS

Apparently the ability of NAFC to decompose with the formation of phenylene and azophenylene radicals can be used for the synthesis of carborane-containing copolymers on the basis of monomers polymerizable via radical mechanism. Earlier [6, 7] we described the synthesis and properties of polystyrene and polyazophenylene copolymers (BS). To reveal the influence of carborane units on the inhibiting activity of polyazophenylene fragments in the processes of thermo-oxidative destruction of polystyrene, we synthesized [9] polystyrene-PAFC copolymers by means of emulsion copolymerization of styrene with NAFC decomposition products. The initial concentration of

NAFC was in the range 0.25-1.1 mole % (based on styrene). Powder-like brown polymers were obtained in 7.4-7.8% yield (based on styrene). According to elemental analysis, the copolymers contained 4-38 wt % PAFC fragments.

A shoulder in the electron absorption spectra of copolymers is observed in the region 300-330 nm. A hypsochromic shift of the absorption spectra as compared with those of BS polymers synthesized earlier [6, 7] indicates a decrease in degree of conjugation when carborane units are introduced into the polyazophenylene fragments.

On the basis of elemental analysis and IR and electron spectra, the following structure I has been attributed [9] to the synthesized copolymers.



I

A study of thermooxidative stability of copolymers FCS by DTA has demonstrated that the introduction of PAFC fragments in the polystyrene macromolecules considerably increases polymer thermostability. While an intense decomposition of polystyrene begins at 300°C (Fig. 5), FCS copolymer, containing 4% PAFC fragments, decomposes at 350-360°C. A comparison of thermooxidative stability of copolymers FCS and BS shows that the introduction of carborane units in polyazophenylene fragments has no influence on the inhibited destruction of copolymers, which is determined by inhibiting action of polyconjugated system and retardation of the depolymerization processes [10].

At 400-450°C a decrease in rate of decomposition of FCS copolymers is observed as compared with BS copolymers. This confirms the above conclusion about the possibility of using carborane-containing compounds for the inhibition of thermooxidative decomposition of polymers at high temperatures.

USE OF PAFC AS A STABILIZER FOR THERMOSTABLE POLYMERS

The propensity of PAFC to add oxygen with the formation of inactive products was used for the inhibition of high temperature decomposition of naphthalene-benzene copolymer (NB), the polybenzoxazole

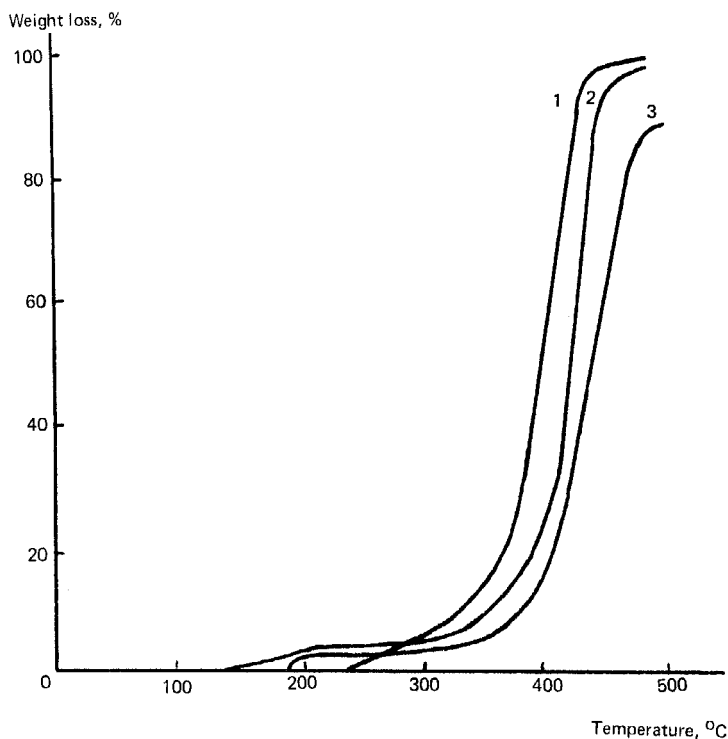


FIG. 5. Dynamic thermogravimetric analysis of polymers in air: (1) PS; (2) BS; (3) FCS. Heating rate, $4.5^{\circ}\text{C}/\text{min}$.

(PBO) based on isophthaloyl chloride and 3,3'-dioxy-4,4'-diaminodiphenylmethane, and a polyoxadiazole (POD) from diphenylphthalide-4,4'-dicarboxylic acid and the dihydrazide of isophthalic acid.

Polyconjugated systems are known [1] to possess an elevated thermooxidative stability and to inhibit the process of thermooxidative destruction of various polymers at $200\text{--}300^{\circ}\text{C}$. It is attributed to their ability to retard the radical processes proceeding by the traditional mechanism of transformation of active radicals into inactive products. However, this principle of stabilization does not lead to considerable positive effects at high temperatures ($350\text{--}450^{\circ}\text{C}$) because in this temperature range even the radicals formed from PCC have sufficiently high activity to participate in chain propagation reactions, and the PCC also undergo radical destruction. In other words, PCC used as inhibitors become chain transfer agents at high temperatures. Possessing high thermal stability, PCC nevertheless need stabilization against thermooxidative destruction at high temperatures.

An attempted kinetic description of the mechanism of thermooxidative decomposition of polyarylenes in the presence of carborane-containing inhibitors has been undertaken in this work. This problem is very complicated if one takes into consideration the variety of chemical processes proceeding at 350-450°C, and some necessary simplifications have been made.

The peculiarity of high temperature decomposition is in the role of primary interaction of oxygen with polymer which sharply increases and can even become decisive with the elevation of temperature, whereas the kinetic chainlength decreases. That is why the prevention or retardation of the proper primary initiation step rather than the decrease of kinetic chainlengths becomes the purpose of stabilization by PCC and other thermostable polymers at high temperatures.

The rate of formation of primary radicals is determined by the oxygen concentration in a polymer. Hence, the rate of decomposition at high temperatures in the absence of stabilizer is limited by oxygen diffusion, which depends on the molecular structure of the polymer. The introduction of so-called "non-chain" inhibitors (effective oxygen acceptors) into the system can result in a considerable decrease in the rate of oxygen interaction with the polymer substrate. If the rate of thermal initiation is negligibly low and interaction of the inhibitor with oxygen does not proceed by radical mechanism, the decomposition rate must decrease. In the absence of a depolymerization process the decomposition rate may be expressed as a sum of two decomposition reactions, one of which is related to the interaction of oxygen with the radical products, and the other one is thermal decay of these radicals:

$$\nu = K_d [O_2] [R\cdot] + K_{dt} [R\cdot] \quad (1)$$

where K_d is the rate constant of destruction with the oxygen participation, K_{dt} is the rate constant of purely thermal destruction, $[R]$ and $[O_2]$ are the concentrations of free radicals and oxygen.

If the chains are terminated via radicals recombination, the stationary concentration of active radicals is expressed as

$$[R]_{st} = (W_i/K_t)^{1/2} \quad (2)$$

where the initiation rate is given by $W_i = K_i [P][O_2]$, and $[P]$ is the concentration of polymer substrate, i. e., of its groups interacting with oxygen. The presence of a "non-chain" inhibitor leads to the decrease of oxygen equilibrium concentration; the relation between the initiation rates in the absence and in the presence of inhibitor may be represented as

$$\begin{aligned} W_{i0}/W_{ix} &= K_i[P][O_2]_0/K_i[P][O_2]_x \\ &= [O_2]_0/[O_2]_x \end{aligned} \quad (3)$$

In a stationary process (when the rates of oxygen diffusion and consumption in chemical reactions are equal) the oxygen concentrations for inhibited and uninhibited process can be expressed as

$$[O_2]_0 = v_{\text{dif}}/(K_i[P] + K_d[R\cdot]_0) \quad (4a)$$

and

$$[O_2]_x = v_{\text{dif}}/(K_i[P] + K_d[R\cdot]_x + K_{\text{inh}}[B]) \quad (4b)$$

where K_{inh} is the inhibition rate constant, and $[B]$ is the inhibitor concentration.

Hence

$$\begin{aligned} [O_2]_0/[O_2]_x &= (K_i[P] + K_{\text{inh}}[B] + K_d k_t^{-1/2} W_{ix}^{1/2}) / (K_i[P] \\ &\quad + K_d k_t^{-1/2} W_{i0}^{1/2}) \end{aligned} \quad (5)$$

Naturally, $[O_2]$ signifies an average oxygen concentration in the reaction zone volume.

The relation between the destruction rates in the presence and in the absence of an effective inhibitor is expressed as in Eq. (6).

$$\begin{aligned} \frac{v_x}{v_0} &= \frac{K_d[R\cdot]_x[O_2] + K_{dt}[R\cdot]_x}{K_d[R\cdot]_0[O_2]_0 + K_{dt}[R\cdot]_0} \\ &= \frac{[R\cdot]_x}{[R\cdot]_0} \frac{K_d[O_2]_x + K_{dt}}{K_d[O_2]_0 + K_{dt}} \\ &= \left(\frac{[O_2]_x}{[O_2]_0} \right)^{1/2} \frac{K_d[O_2]_x + K_{dt}}{K_d[O_2]_0 + K_{dt}} \end{aligned} \quad (6)$$

If the thermal destruction rate in the presence of an inhibitor is considerably higher than that of the thermooxidative destruction, i. e.,

$K_{dt} \gg K_d[O_2]_x$, and the rate of the oxygen consumption in the inhibition reaction is much higher than the sum of the oxygen consumption in the initiation of the thermooxidative destruction and the chain propagation reaction, i. e.,

$$K_{inh}[B] \gg K_i[P] + K_d \cdot K_t^{-1/2} W_{ix}^{1/2} \tag{7}$$

then Eq. (6) is transformed into Eq. (8):

$$v_0/v_x = ([O_2]_0/[O_2]_x)^{1/2} \{1 + (K_d[O_2]_0/K_{dt})\} \tag{8}$$

Since

$$\begin{aligned} \frac{[O_2]_x}{[O_2]_0} &= \frac{K_i[P] + K_d K_t^{-1/2} W_{io}^{1/2}}{K_{inh}[B]} \\ &= \frac{1 + K_d K_t^{-1/2} K_i^{-1} W_{io}^{1/2} [P]^{-1}}{K_{inh} K_i^{-1} [P]^{-1} [B]} \end{aligned} \tag{9}$$

one can obtain:

$$[O_2]_x/[O_2]_0 = ([P]/[B]) K \tag{10}$$

where

$$K = \frac{1 + K_d K_t^{-1/2} K_i^{-1/2} W_{io} [P]^{-1}}{K_{inh} K_i^{-1}} \tag{11}$$

Substituting this expression into Eq. (9) yields Eq. (12):

$$(v_x/v_0)([B]/[P])^{1/2} = K^{1/2} \{1 + (K_d[O_2]/K_{dt})\}^{-1} = \text{const} \tag{12}$$

Thus, in the range of elevated inhibitor concentrations a straight line parallel to the abscissa must be observed in the coordinates

$$(v_x/v_0)([B]/[P])^{1/2} = f([B]) \tag{13}$$

The kinetic equations were verified experimentally by using PAFC

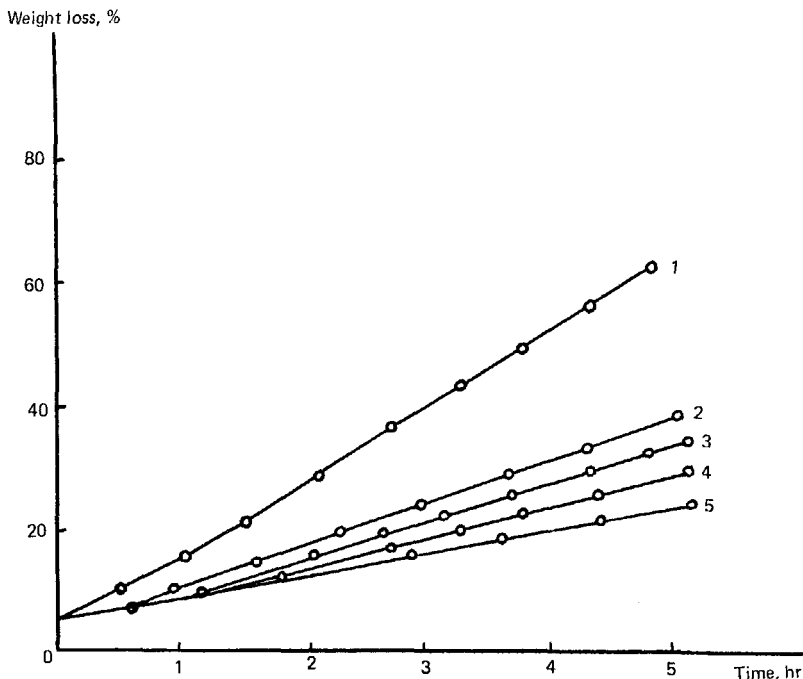


FIG. 6. Isothermic thermogravimetric analysis of crosslinked NB compositions in air at 400°C: (1) NB; (2) NB + 10% PAFC; (3) NB + 15% PAFC; (4) NB + 20% PAFC; (5) NB + 25% PAFC.

as an inhibitor and aromatic polymer as a substrate. The PAFC distribution in the polymer was achieved by mixing the polymer and PAFC solutions, with subsequent coprecipitation [in the case of naphthalene-benzene copolymer (NB)] or by the introduction of PAFC into the concentrated solutions of prepolymers (POD or PBO) with the subsequent distillation of the solvent and cyclization of prepolymer.

The decomposition of NB crosslinked by aromatic oligomers based on p-xylyleneglycol was carried out in the air at 400 and 450°C under isothermal conditions at a PAFC concentration of 10-25%.

The data obtained demonstrate (Figs. 6 and 7) that PAFC considerably decreases the rate of the process, whereas there is practically no stabilizing effect in an inert atmosphere. After the initial non-stationary stage characterized by the elevated rates, the process becomes stationary.

Analogous results were obtained with noncrosslinked copolymers. In this case the initial weight losses were some higher; however the polymer rapidly became insoluble, and acquired a crosslinked

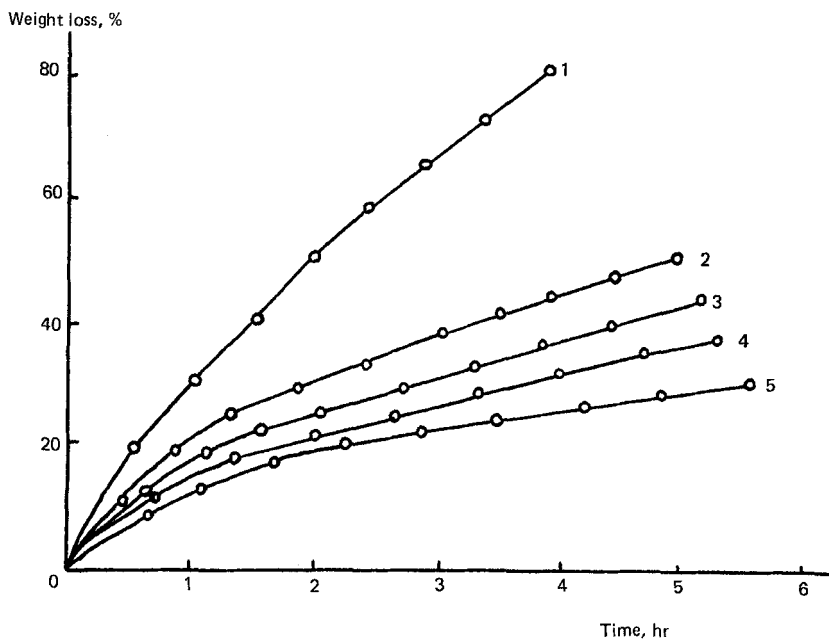


FIG. 7. Isothermic thermogravimetric analysis of crosslinked NB composition in the air at 450°C : (1) NB; (2) NB + 10% PAFC; (3) NB + 15% PAFC; (4) NB + 20% PAFC; (5) NB + 25% PAFC.

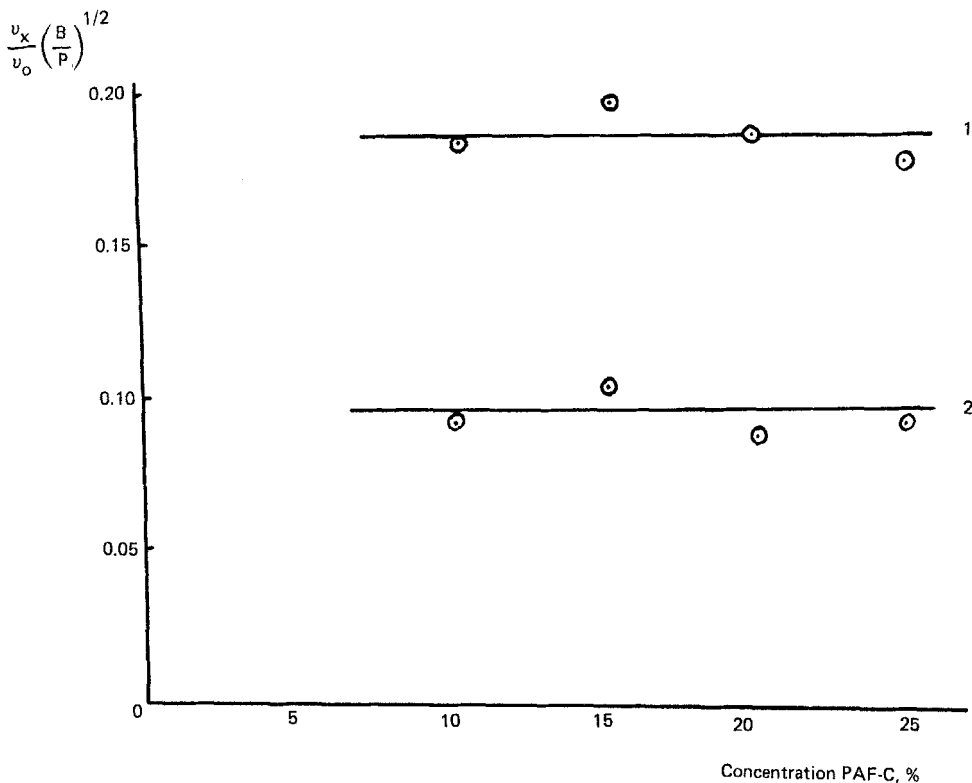


FIG. 8. The dependence $(W_x/W_0)([B]/[P])^{1/2}$ vs. [PAFC]: (1) 450°C; (2) 400°C.

structure; its further behavior was the same as that of the previously crosslinked polymer.

As may be seen from Fig. 8, where the experimental data are presented at $(V_x/V_0)([B]/[P])^{1/2} = f([B])$, the kinetic data are in good agreement with Eq. (12) deduced on the basis of the supposition about the concurrence of reactions of initiation and oxidation of carborane-containing stabilizer. The linear dependences are parallel to the abscissa.

It is impossible to evaluate the values of Arrhenius coefficients for any rate constant because of complexity of the parameter $K^{1/2}(1 + K_{dt}^{-1}K_d[O_2])^{-1}$.

Thus the complex processes of inhibited thermooxidative decomposition of thermostable polymers may be expressed by a rather simple kinetic equation.

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