JOURNAL OF CATALYSIS 13, 261–270 (1969)

Heterogeneous Catalysis on Organic Conjugated Polymers

II. Electron Spin Resonance and Structural Factor

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Received April 9, 1968; revised October 15, 1968

Various structural properties were recently discovered to be significant for the catalytic activity of the paramagnetic centers in conjugated polymers. Most of them have been discussed elsewhere, but the results of this paper suggests that nearly all of them may be explained by a more general factor, namely, the exchange interactions of the free spins brought about by structural rearrangements preceding graphitization. The appearance of such exchange interactions is accompanied by the decay of the intrinsic catalytic activity of the free spins. The observed tendency of heteroatoms to favor the catalytic activity is thus explained by their role in hindering graphitization, a phenomenon well known in "cold carbons."

1. INTRODUCTION

In previous communications, we established that free spins (unpaired electrons) in conjugated polymers play an essential role in catalytic processes such as dehydrogenation of alcohols and decomposition of nitrous oxide (*1*, *2*).

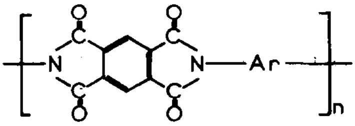
Nevertheless, in studying the catalytic properties of a family of polymers, polyacene-quinones, obtained by the method described by Pohl (*3*), we pointed out that, although the number of free spins in each member of this family was the same, their catalytic activity in the decomposition of formic acid was different. These results emphasized the role of a factor related to the chemical structure of the polymers. One of us, in a thesis dissertation, showed a good correlation between the dehydrogenation activity of various polyacene-quinone polymers and the number of quinoid ring functional groups they contain (*7*).

The bearing of the structure of conjugated polymers on their catalytic activity has since been investigated by Manassen and co-workers (*4*, *5*, *6*). These authors, in inserting different functional groups in the polymers, disclosed good correlations between the presence of those groups and the catalytic behavior of this particular kind of conjugated polymers (*6*). In the case of polymers belonging to another family and known as pyromellitimides, initial results on the catalytic activity in the decomposition of nitrous oxide also gave evidence of a structural factor (*1*).

In the family of polyacene-quinones, the number of spins of each member was the same and the properties of the spins were quite similar. On the contrary, in the family of pyromellitimides as well as in other families which do not contain special functional groups, we observed that the properties of the spins were largely different from one member to the other of a given family. Our aim was to investigate the connections between several properties of the spins—including catalytic activity—and the structure of the polymers carrying them.

Two lines of investigation were followed. First we studied the influence of heat-treatment on the properties of the free spins in several polymers: this study was carried out with the collaboration of other workers (*8*). Secondly, we compared various polymers, as well-defined as possible and treated at a temperature sufficiently low not to modify their structure. In order not to change too

POLYPYROMELLITIMIDES



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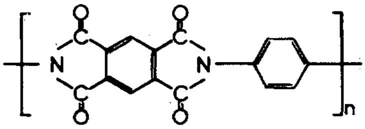
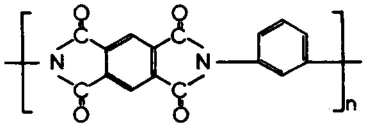
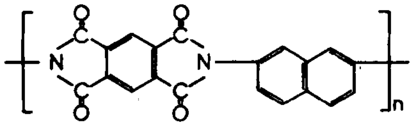
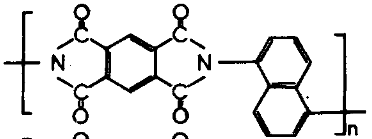
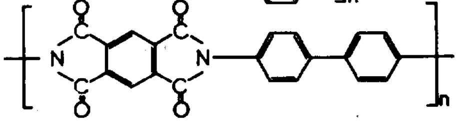
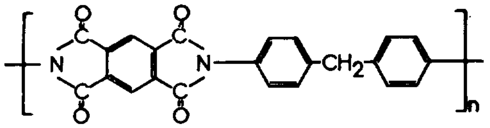
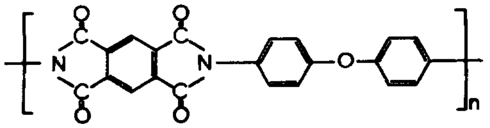
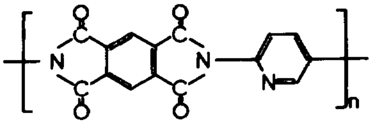
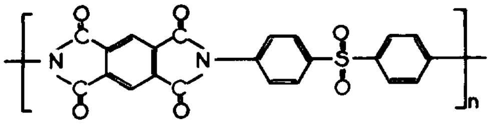
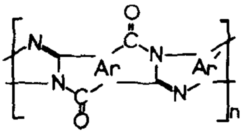
	400° C	1
	400°C	2
	400° C	3
	400°C	4
	400°C	5
	400°C	6
	400°c	7
	400°C	8
	400°C	9

FIG. 1. Polypyromellitimide family: 1st column; polymer; 2nd column, temperature of heat-treatment in argon; 3rd column, reference number of the polymer.

many chemical structural factors simultaneously, the polymers were chosen in only two families. For additional discussion, other polymers, belonging to other families were also used. The role of the structure was studied in relation both to the properties of the free spins and to the catalytic activity.

Rapid mention will be made of a number of results already published, but the discussion will concentrate on new results

POLYINDOLOIMIDAZOLES



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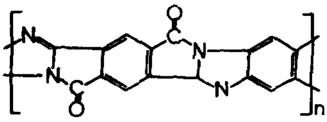
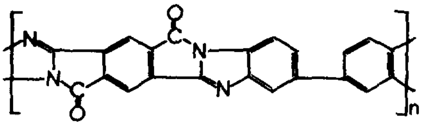
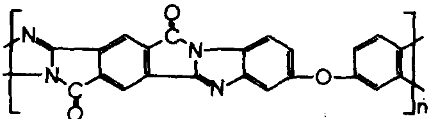
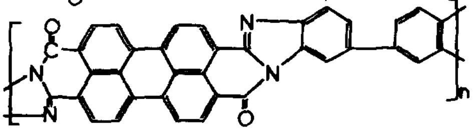
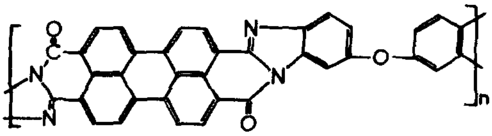
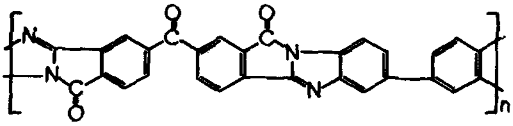
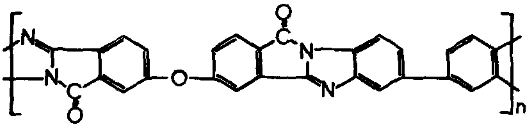
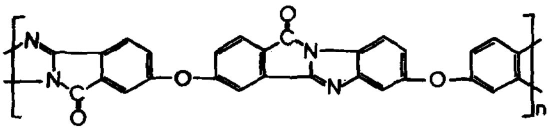
	350°C 400°C	10 11
	350°C	12
	400°C	13
	350°C	14
	400°C	15
	350°C	16
	350°C 400°C	17 18
	400°C	19

FIG. 2. Polyindoloimidazole family.

CROSSLINKED POLYMERS

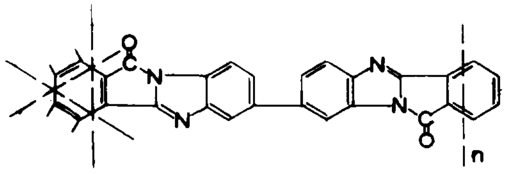
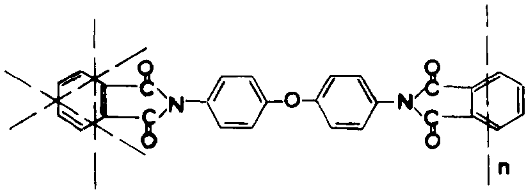
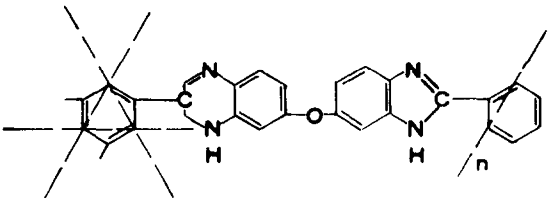
Polymers	Temperature of heat treatment	Number of polymer
	380° C	20
	380° C	21
	380° C	22

Fig. 3. Cross-linked polymers.

concerning the role of exchange interactions susceptible to impede the catalytic action of the free spins and on the possible factors governing these exchange interactions.

2. Experimental

Polymers. The various polymers investigated are graphically represented in Figs. 1, 2, and 3. The synthesis of the first two families—polypyromellitimides (*9*) and polyindoloimidazoles (*10, 11*)—has been described elsewhere. In the third group (Fig. 3) polymers are characterized by the presence of cross-linkings; they belong to three different families: polypyromellitimide (polymer 20), polyindoloimidazole (polymer 21), and polybenzimidazole (polymer 22).

The polyimide and polyindoloimidazole are obtained by liquid condensation of mellitic anhydride with, respectively, diamino-4,4′-diphenyl ether and diamino-3, 3′-benzidine. The prepolymers obtained in dimethylformamide are then cyclized by heat-treatment under argon at 260°C during 24 hr. Thermogravimetric measurements of the release of water vapor occurring during the cyclization reaction show that this treatment is necessary for the complete cyclization of the product.

The benzimidazole cross-linked polymer

is obtained by a condensation reaction between trimesic acid and 3,4,3′,4′-tetraminodiphenyl ether. The reaction is carried out under argon in polyphosphoric acid at about 210°C.

Catalytic reaction. The catalytic reaction used throughout the present work is the decomposition of nitrous oxide. The experimental technique has been previously described (*12*).

The experimental conditions for the catalytic measurements, as well as those for the heat-treatment of the polymers, are indicated in the appropriate tables.

The catalytic activity is the initial rate of the reaction expressed in mole m^{-2} sec^{-1}. The catalytic activity of the free spin, which we call intrinsic activity of the free spin and refer as A, is the ratio of the catalytic activity calculated at 650 mm of Hg and 400°C (first order reaction) to the concentration of the free spins in the samples.

Paramagnetic resonance. All measurements were performed with a Varian, Model V 4501 spectrometer. The determination of the free spin concentration N was made as explained in ref. (*13*). Relaxation times T_1 were evaluated by the saturation method (*14*).

3. Results and Discussion

The first polymers we investigated are tabulated in Figs. 1 and 2. Table 1, presenting the results of the catalytic tests, shows clearly that the various polymers constitute two distinct classes differentiated by the value of the activation energy of the catalytic reaction which they bring about. In one class (4 from the polyindoloimidazole family), the activation energy E is about 20–25 kcal $mole^{-1}$, while in the other (the members of the family of pyromellitimides and 4 from the polyindoloimidazole fay)ilm E is between 40 and 50 kcal $mole^{-1}$.

The former class contains all the polymers characterized by a regular uninterrupted alternation of single (σ) and double ($\pi + \sigma$) bonds. Polymer number 16 with a carbonyl group is considered to belong to this class. In the second class, the alternation of ($\pi + \sigma$) and (σ) bonds is periodically interrupted by N or O atoms. For the sake of simplicity we call these classes, respectively the perfectly and imperfectly conjugated polymers.

TABLE 1
Catalytic Test Results

Polymer	Concentration of the free spins	T (°C)	Initial pressure of N_2O (mm Hg)	Catalytic activity (mole m^{-2} s^{-1})	E (kcal $mole^{-1}$)	Catalytic activity of the free spins A
1	2×10^{17}	400°	370	3.5×10^{-9}	—	30
2	2×10^{17}	400°	370	3.4×10^{-9}	—	30
3	8×10^{17}	400°	370	1.5×10^{-7}	48 ± 4	320
4	9×10^{18}	400°	370	1.1×10^{-7} mole g^{-1} s^{-1}	48 ± 4	Surface area <1 m^2
5	$<10^{16}$	400°	370	3.1×10^{-9}	48 ± 4	>540
6	1.3×10^{18}	400°	370	1.2×10^{-7}	—	160
7	3.5×10^{17}	400°	370	1.2×10^{-8}	—	60
8	3×10^{17}	400°	370	2.6×10^{-11}		Zero order reaction
9	$<10^{17}$	Unstable polymer at the temperature of the catalytic activity test				
10	4×10^{18}	360°	630	9.7×10^{-8}	28 ± 3	500
11	4×10^{18}	360°	630	6.7×10^{-8}	23 ± 1	50
12	1.9×10^{17}	360°	630	2×10^{-10}	18 ± 4	2
14	2.1×10^{19}	360°	630	4.9×10^{-11}	27 ± 2	0.05
16	2.8×10^{18}	360°	630	6.5×10^{-9}	21 ± 2	6
19	9.5×10^{18}	400°	650	1.2×10^{-8}	40 ± 2	1
13	1.0×10^{18}	400°	650	1.9×10^{-9}	43 ± 3	2
15	2.3×10^{18}	400°	650	9.1×10^{-8}	40 ± 2	4
18	1.7×10^{18}	400°	650	9.6×10^{-8} mole g^{-1} s^{-1}	44 ± 2	—
17	2×10^{18}	360°	630	2.3×10^{-10}	52 ± 4	0.3

The two orders of magnitude of activation energies differenciating these two distinct classes have been rigorously observed for all of the nearly 30 polymers we have studied until now.

The various structural factors one can investigate comparing different polymers have been discussed elsewhere, in particular the linear relation between the intrinsic activity of the free spin and the number of bonds between two interruptions of conjugation in imperfectly conjugated polymers (*15*). One factor appearing to merit further examination was the role of heteroatoms in perfectly conjugated polymers. This factor gives indeed an insight into the properties a polymer must possess in order to be active.

The following discussion will be centered on this role and on its explanation, taking into account the properties of the free spins involved in catalysis.

The starting point of the present work is the observation that the catalytic activity in perfectly conjugated polymers depends upon the ratio of the number of carbon atoms to the total number of atoms in the chain, namely carbon, nitrogen and oxygen atoms, hydrogen being excluded (Fig. 4). This ratio will be expressed by C/(C + N + O). Thus, the higher the heteroatom content, the higher the catalytic activity. It is worth mentioning that three other polymers belonging to three families other than those studied here obey this law; this relation is supported by the good activity of pyrolyzed polyacrylonitrile, the most likely structure of which is that of a ladder polymer in which there is one N atom for three C atoms.

To understand the influence of the heteroatoms on the catalytic activity of the free spins of the perfectly conjugated polymers, we must take a closer look at the properties of the free spins of the conjugated polymers.

In a previous communication (*1*) we mentioned a parallel between the catalytic

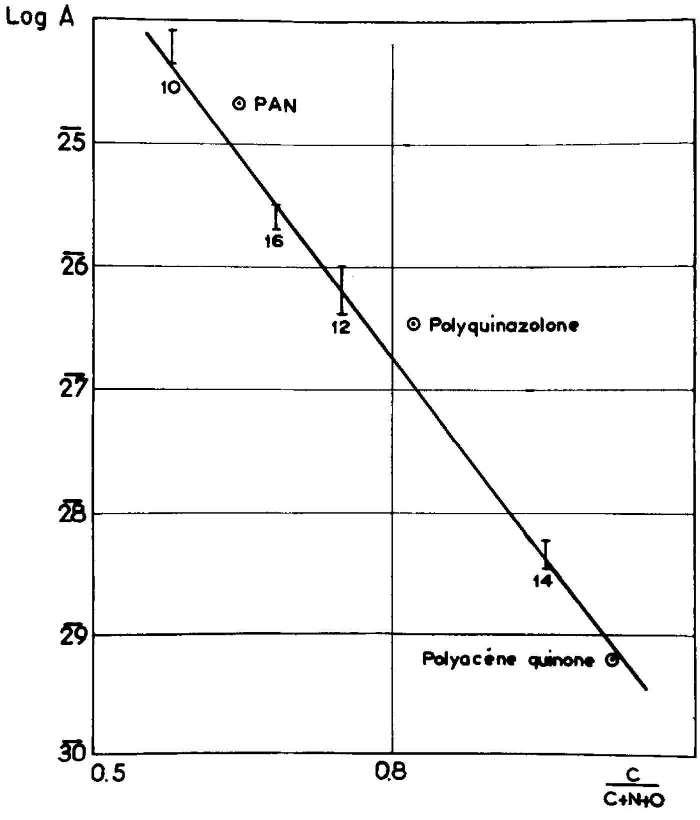


FIG. 4. Logarithm of the catalytic activity of the free spins A versus C/(C + N + O).

activity and the number of free spins in the conjugated polymers treated at various temperatures. However, the intrinsic activity of the free spins was not constant. An explanation of this could be that not all free spins are really active in catalysis, the properties of the free spins varying with the heat-treatment. For example, in the case of polyacrylonitrile, the overall catalytic activity, or activity per gram (curve 1 of Figure 5) could be considered as due to a combined effect of the number of spins represented by the experimental curve 2, and their intrinsic catalytic activity. In order to account for the experimental curve 1, the intrinsic catalytic activity must be represented by the curve 3.

This explanation seems to be very likely, since measurements directly related to the specific properties of the spins, namely, the width of the EPR line, ΔH, and the relaxation time T_1, show variations very similar to those anticipated for the intrinsic catalytic activity of the spins. For the sake of clarity, we have plotted only the curve of variation of ΔH (curve 4) since as one can see on Fig. 6, that of T_1 is similar. In this figure are plotted, together with the intrinsic activity (activity per free spin), the experimental width ΔH of the EPR line and the relaxation time T_1 versus the temperature of heat-treatment θ. A close connection is observed between the intrinsic activity A and the relaxation time T_1.

The correlation not only holds for the activity of the free spins in a series of catalysts obtained by heating a given polymer at different temperatures, but also for nearly all the polymers we studied and particularly for the 14 polymers of the present families for which A could be calculated (*8*).

Thus, the catalytic intrinsic activity of the spins of polymers, perfectly as well as imperfectly conjugated, appears to be a

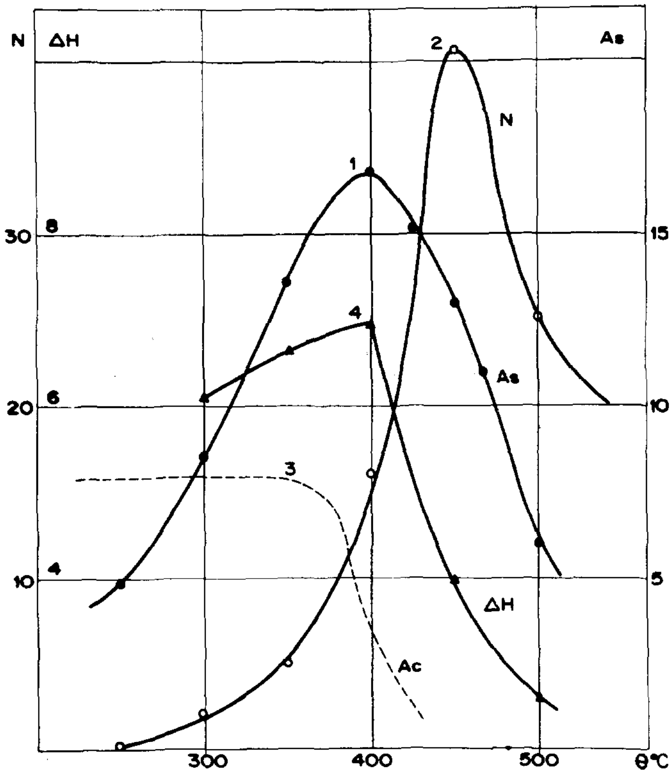


FIG. 5. Variations of the specific number of spin, N (arbitrary units); the width of the ERP line, ΔH (gauss); the activity per gram, A_s; and the intrinsic activity of the free spins, A_c versus temperature of heat-treatment θ (°C) in the polyacrylonitrile polymer.

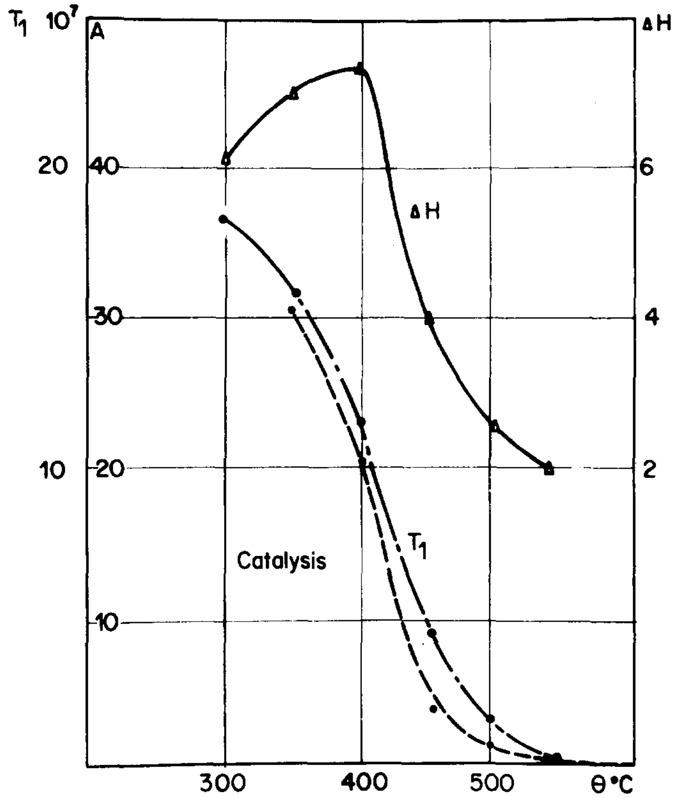


FIG. 6. Variations of the specific activity of the free spins, A; the width of the EPR line, ΔH (gauss); and the relaxation time, T_1 (sec) versus heat-treatment θ (°C) in the polyacrylonitrile polymer.

statistically growing function of the relaxation time T_1.

There is much evidence to ascribe the sudden decrease of ΔH as well as of T_1 to the appearance of exchange interactions (*16, 17*). A similar evolution of ΔH and T_1 is observed in pyrolyzed "cold carbons" (*18*) and it is generally postulated that it is due to structural modifications such as the appearance of cross-linkings between carbon chains (*1*).*9*

In order to investigate whether this factor could be operative in our case, we synthesized the three cross-linked polymers listed on Fig. 3. Figure 7 gives the variations of N (number of free spins per gram), ΔH, and T_1 as a function of the temperature of heat-treatment θ for the cross-linked polymer number 22. Clearly ΔH is too great (from 6 to 8 gauss) to be compatible with exchange interactions. Similar conclusions arise from the results obtained with both other cross-linked polymers. On the other hand, there is no difference in catalytic activity between a cross-linked polymer and its linear homolog (see the two last columns of Table 2).

An important result which leads us to a more likely explanation of the role of heteroatoms in perfectly conjugated polymers is that the temperature above which ΔH and T_1 begin to decrease rapidly is higher for the cross-linked polymers than for the linear ones. An interpretation of this result, given by Nechtschein (20), is that the exchange interactions appear simultaneously with the formation of pregraphitized flat zones: cross-linkings giving a higher stiffness to the macromolecule might hinder the graphitization process.

In the different conjugated polymers, for which we found a correlation between the catalytic activity and T_1, the decrease of T_1 could account for the degree of exchange interactions which, according to the above

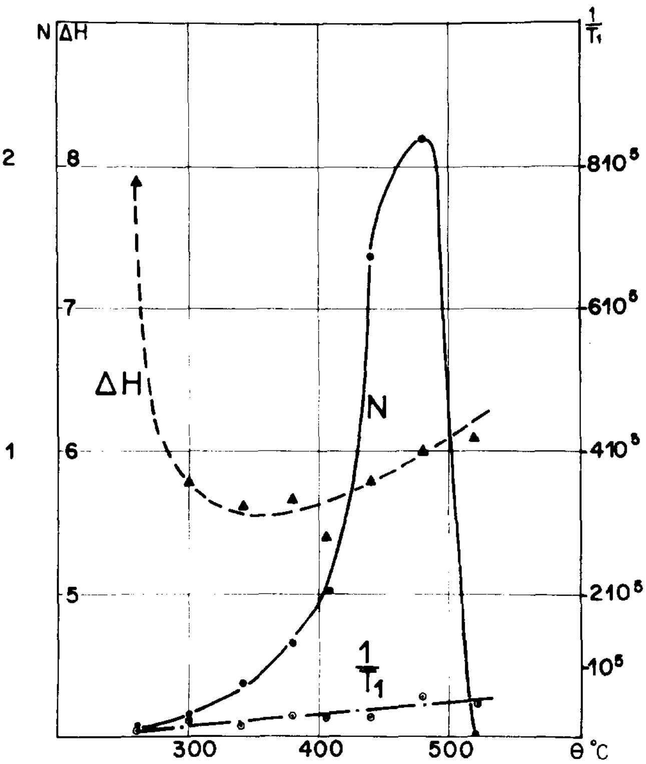


FIG. 7. Variations of the number of spins, N (arbitrary units); the width of the EPR line, ΔH (gauss); and the relaxation time, T_1 (sec) versus heat-treatment in the polybenzimidazole cross-linked polymer.

hypothetsis, would be the consequence of graphitelike arrangements.

It is known that in "cold carbons" the presence of heteroatoms delays the graphitization process (*21*, *22*). They might play the same role in conjugated polymers. As we know that graphite is inactive in nitrous oxide decomposition, we can assume that the more the polymer is graphitizable, the smaller its catalytic activity. This gives a quite good account of the dependence of A on the ratio C/(C + N + O).

We thus arrive at an interpretation following which many differences in catalytic properties of the free spins of various conjugated polymers are not the consequence of definite structural characters of the macromolecules but are rather due to the tendency of their structure to graphitize or, at least, to arrange in a crystalline manner. This is supported by results obtained from a polyacene-quinone for which the C/(C + N + O) ratio is very high. It is one of the least-active polymers. Using X-ray diffraction we succeeded in demonstrating the presence of small graphitized domains in this polymer.

TABLE 2
CATALYTIC ACTIVITY OF CROSS-LINKED POLYMERS

Polymer	Free spins $\times 10^{18}$	T (°C)	Initial pressure of N_2O (mm Hg)	Catalytic activity $\times 10^{-9}$	E	A	A in the corresp. linear polymer
20	5.8	360°	630	5.8	18 ± 4	10^{-27}	10^{-27}
21	0.7	375°	370	2.9	—	4×10^{-27}	8.6×10^{-27}
22	28	360°	630	28×10^{-8}	32 ± 1	10^{-27}	8.7×10^{-28}

CONCLUSION

The previously published results together with the present paper sum up the correlations found up to now between structural factors and catalytic activity of polymers, perfectly, as well as imperfectly conjugated. They also give precise correlations between catalytic activity and properties of the free spins in these polymers. Up to now, many partial conclusions have been stated concerning the catalytic activity of polymers. Various theoretical explanations have been suggested (*23*, *24*, *25*). As far as our own work is concerned, the emphasis has been laid mainly on the experimentals facts. At least, we obtain a better view of what is the best polymer with the highest catalytic activity in nitrous oxide decomposition: a perfectly conjugated polymer, with as many heteroatoms as possible, treated at a temperature slightly below that at which the exchange interactions begin to be noticeable.

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