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THERMAL STUDIES OF SOME SUBSTITUTED POLY-*N*-VINYLCARBAZOLES

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ABSTRACT

Thermal properties of polymers based on poly-*N*-vinylcarbazole containing substituents such as halogen, methyl, methoxy and acetyl groups were investigated using thermogravimetric and differential thermal analytic techniques. Kinetic parameters of the thermal degradation process were determined by means of numerical methods of estimation. Preliminary analyses of the volatile degradation products were carried out using the combined methods of pyrolysis and gas chromatography.

INTRODUCTION

Thermal properties of polymers as well the processes of their thermal degradation have been investigated widely and are the subject of many works [1–4]. Such studies supply information about fundamental degradation reactions, and provide indications concerning the processing, utilization and storage of polymeric materials. Of the various techniques used for the estimation of thermal properties of polymers, thermogravimetry (TG) and differential thermal analysis (DTA) have turned out to be particularly useful [2].

In the present work, these two techniques were applied in the investigation of a series of polymers based on poly-*N*-vinylcarbazole (PNVC), to characterize their thermal behaviour. PNVC belongs to a group of polymers which exhibit outstanding thermal stability, its glass transition point T_g being the highest among vinyl polymers [5]. The thermal degradation of PNVC has been described by Barrales et al. [6] and Stolka [7]. The present work attempts to evaluate the influence of different substitutents introduced into the carbazole ring during the process of thermal degradation.

EXPERIMENTAL

Materials

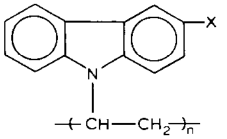
The monomers and polymers were prepared according to the method of Chrzaszcz [8]. The monomers were polymerized radically in DMF solution using AIBN as the initiator, at 60 °C for 8 h. The polymers were then precipitated and the residual monomers removed by repeated extraction from methanol.

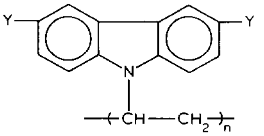
Techniques

Thermal studies were carried out using a Mettler TA-2 apparatus (Switzerland). The measurements were carried out at a heating rate of 3° min^{-1}, with a sample weight of ca. 50 mg, in inert (argon) and oxidative (air) atmospheres. Al_2O_3 was used as the inert material. Pyrolysis and gas chromatography were carried out using a Carlo–Erba Model GV gas chromatograph with a flame ionization detection system, connected to a pyrolyser of the filament type. The gas chromatographic separation was performed on a 2.8 m × 2 mm I.D. steel column packed with 10% UCCW 982 on Chromosorb W AW DMCS 80/100 mesh. The argon flow rate was 30 ml min^{-1}. In a separate series of experiments, the separation was performed on a 4 m × 2 mm I.D. steel column packed with 20% polyphenyl ether on Chromosorb P 60/80 mesh, and a 5 m × 2 mm I.D. steel column packed with 1,2,3-tricyanoethoxypropane on Al_2O_3, in weight ratio 27 : 100. The argon flow rate was 40 ml min^{-1}.

RESULTS AND DISCUSSION

The polymers under investigation were of the general formula





where : $X = Cl, Br, I, CH_3, OCH_3$; $Y = Cl, Br, I, COCH_3$

The polymers contained substituents of varying electronegativity and inductive effect. It was therefore expected that the interaction between these substituents and the electron system of the carbazole ring, and the main vinyl chain would lead to differences in the thermal degradation process; and the results of TG measurements did indeed reveal significant differences

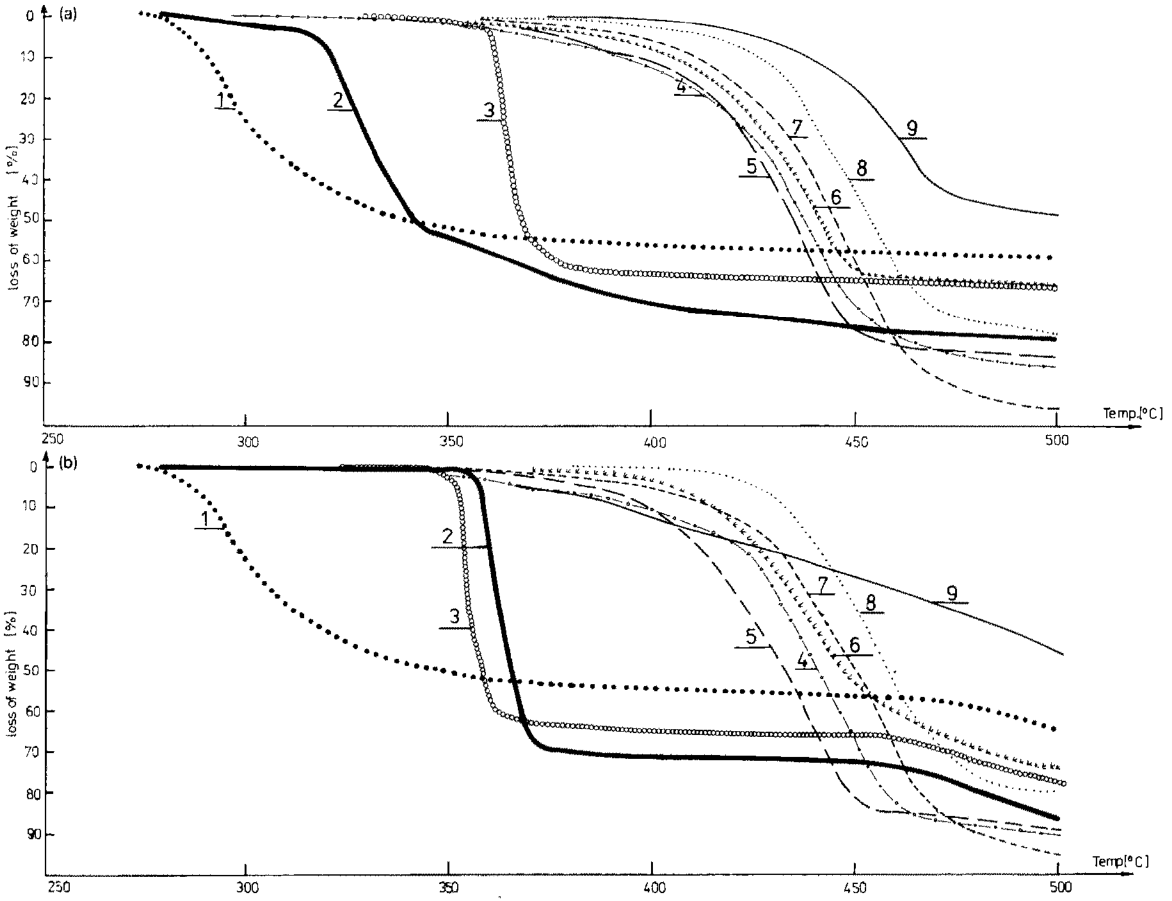


Fig. 1. The dependence of weight loss on temperature for the substituted poly-*N*-vinylcarbazole: (a) in the inert atmosphere, argon; (b) in the oxidative atmosphere, air. Key: (1) 3-iodo; (2) 3-bromo; (3) 3,6-dibromo; (4) 3-chloro; (5) 3,6-dichloro; (6) 3-methoxy; (7) PNVC; (8) 3-methyl; (9) 3,6-diacetyl.

between the thermal stabilities of the polymers studied [9,10]. The dependence of weight loss on temperature for these polymers is shown in Fig. 1.

As can be seen, the initial decomposition temperature (IDT) of the process varied remarkably among the polymers studied, the lowest being that for the 3-iodo derivative (250 ° C) and the highest that for the 3,6-diacetyl derivative (378 ° C), for the measurements carried out in the inert atmosphere. In the oxidative atmosphere the iodinated PNVC turned out to be the most unstable material (IDT = 256 ° C), while the methyl derivative was stable up to 408 ° C. The decline in the thermal stability of the acetyl derivatives in the presence of air is probably due to oxidative reactions of the acetyl group.

In order of increasing IDT value, the polymers investigated are as follows

$$\text{3-I–} < \text{3-Br–} < \text{3,6-Br–} < \text{3-Cl–} < \text{3,6-Cl–} < \text{3-OCH}_3\text{–} < \text{PNVC} < \text{3-CH}_3\text{–} < \text{3,6-COCH}_3\text{–}$$

in an inert atmosphere, and

$$\text{3-I–} < \text{3-Br–} < \text{3-Cl–} < \text{3,6-Cl–} < \text{3,6-COCH}_3\text{–} < \text{3,6-Br–} < \text{3-OCH}_3\text{–} < \text{3-CH}_3\text{–}$$

in an oxidative atmosphere.

The thermal effects which accompanied the degradation processes were observed on DTA curves. The DTA curves for the polymers studied showed that endothermal effects were predominant for decomposition in both the oxidative and the inert atmosphere, except for the iodo derivatives (in both atmospheres) and the acetyl derivative (in the oxidative atmosphere). The exception of the acetyl derivative could be related to the susceptibility of the acetyl group to oxidative reaction. The exception of iodinated PNVC is probably connected with the mechanism of the decomposition.

TABLE 1

Temperatures of maximum thermal effect (DTA curve) and decomposition rate (DTG curve)

No.	Polymer PNVC derivative	Temperature DTA (° C)		Temperature DTG (° C)	
		Air	Argon	Air	Argon
1	3-iodo	295 [a]	291 [a]	295	291
2	3,6-dibromo	352	369	355	369
3	3-bromo	360	382	360	382
4	3,6-dichloro	441	437	439	437
5	3-chloro	441	441	445	440
6	3-methyl	453	450	456	454
7	3-methoxy	435	453	435	439
8	PNVC	458	458	458	456
9	3,6-diacetyl	429 [a]	461	395	461

[a] Exothermal effects.

TABLE 2

The estimated values of the kinetic parameters (atm.: air) activation energy E_a, absolute rate constant A, and reaction order n

No.	Derivative of PNVC	E_a (kcal mol^{-1})	A (s^{-1})	n
1	3,6-dichloro	34.3	2.54×10^{13}	1
2	3-chloro	37.4	1.73×10^{9}	0.55
3	3-methoxy	41.6	4.87×10^{10}	0.19
4	PNVC	47.8	1.70×10^{11}	0.73
5	3,6-diacetyl	51.2	8.73×10^{15}	0.75
6	3-methyl	59.9	7.15×10^{14}	0.58
7	3-bromo [a]	–	–	–
8	3,6-dibromo [a]	–	–	–

[a] Both cases impossible to calculate according to the accepted procedure from a mathematical point of view, i.e. the rapid loss of weight occurring in very narrow temperature range (5–8 ° C).

The temperatures of maximum thermal effect ($T_{\max}$) and maximum decomposition rate ($T_{R\,\max}$, determined from DTG curves) are compiled in Table 1.

As can be seen, the $T_{\max}$ values of the polymers increase in a similar order as for IDT value, and this order corresponds to that for $T_{R\,\max}$.

The kinetic parameters of the thermal degradation processes, i.e. activation energy, absolute rate constant and reaction order, were computed using numerical methods of estimation [11]. The values of the kinetic parameters are presented in Table 2.

Pyrolysis and gas chromatography studies

In considering the thermal stability of a series of halogenated polymers, it was noticed that their IDT values increased in a sequence which can be correlated with the changing electronegativity of the halogen atom, and carbon–halogen bond dissociation energy, i.e. I < Br < Cl [1]. This implied either that cleavage of the carbon–halogen bond in the carbazole ring takes place at different rates and temperatures, or that the halogen substituent affects the stability of the radicals formed during the degradation process. It was therefore decided to analyse the degradation products in a series of pyrolysis–gas chromatography experiments for PNVC, and the 3,6-dibromo and 3,6-dichloro derivatives.

The pyrolysis was performed at 50 ° C temperature intervals in the range 300–500 ° C. In all cases, two main peaks appeared on the pyrograms. One of these is identified as a peak corresponding to the monomer. The presence of monomers in the pyrolyzates is evidence for the occurrence of depolymerization reactions in the thermal degradation process. On the other hand,

TABLE 3

The ratio of the area under the peaks corresponding to the degradation products (I) and the monomers (II)

No.	Polymer	Ratio of peak areas I/II at temperature (°C)				
		300	350	400	450	500
1	PNVC	1.04	1.19	1.40	1.36	1.57
2	dichloro derivative	0.20	0.28	0.25	0.35	0.49
3	dibromo derivative	–	1.09	–	–	1.49

the presence of the next broad peak indicates that random degradation and destruction processes are also involved. Attempts to resolve this second peak revealed that the following compounds were evolved during the pyrolysis: ethane, ethylene, propylene, C_4-olefins/isobutene, 1,3-butadiene, 2-methylbutadiene, 1,3-*cis*-but-2-ene, *trans*-but-2-ene/*n*-butane, and trace amounts of C_5 and C_6 hydrocarbons. One further peak, which appeared for all samples analysed, remains unidentified.

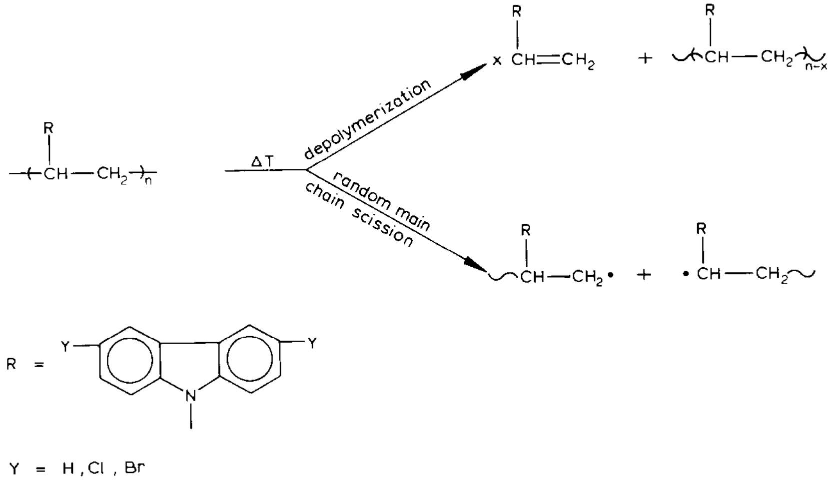
It is likely that the products mentioned above derive from the destruction of monomers formed during depolymerization, and from the polymer chain. The ratio of the areas under the two main peaks for the monomers and other compounds, taken at different temperatures, reflects the progress of degradation and the mutual contribution of these components at various stages of thermal decomposition. The characteristic values are given in Table 3. It was found that the amount of volatile degradation products obtained in relation to the monomer increased with increasing pyrolysis temperature. This can be ascribed to more frequent and complex bond ruptures at higher temperatures.

From the TG, DTA and pyrolysis–GC results obtained so far, it can be concluded that the halogen atom introduced into the carbazole ring influences radical stability. Thus, the higher values of IDT for iodo to chloro derivatives can be related to the increased stability of radicals formed during the depolymerization stage, which would in turn delay the general rate of the decomposition process. One might therefore expect an additive phenomena in the case of di-substituted polymers, but the results did not support this idea, e.g. IDT for the 3-iodo derivative was lower than that for the 3,6-diiodo derivative.

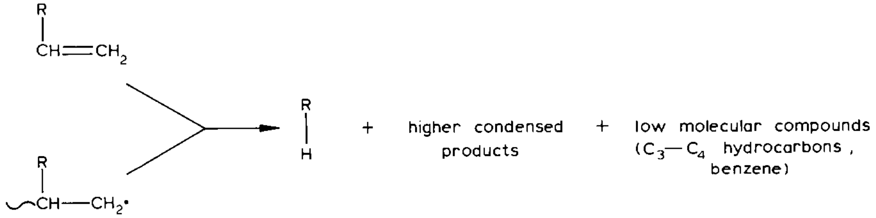
Here morphological factors may play a role, because di-substituted formations are known to be able to create more regular and ordered structures, which are of greater thermal stability, than those of mono-substituted formations [5].

Given our present state of knowledge, the following scheme for the thermal degradation process of halogenated PNVC derivatives can be suggested

Primary reactions: depolymerization, degradation.



Secondary reactions: decomposition of the liberated monomer oligomers and macroradicals.



However, to obtain a detailed description of the thermal degradation process it is still necessary to investigate the influence of molecular weight, size and distribution on thermal properties, as well as the effect of possible structural changes in the temperature range preceding a loss of weight. Such studies are in progress.

CONCLUSION

Thermal properties of the PNVC derivatives synthesized varied remarkably, dependent on the kind of substituent introduced. Methyl, methoxy and acetyl derivatives exhibited higher thermal stability than PNVC itself, while the halogenated forms were less stable. For the halogenated derivatives, the degradation process proceeds via a depolymerization reaction, and partially via random degradation of the main polymer chain.

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