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TGA/FTi.r. studies on the thermal stability of poly(vinyl chloride) blends with a novel colourant and stabilizer: 3-(2,4-dichlorophenylazo)-9-(2,3-epoxypropane)carbazole

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It has been found that 3-(2,4-dichlorophenylazo)-9-(2,3-epoxypropane)carbazole can act as an efficient colourant and thermal stabilizer of poly(vinyl chloride) (PVC). It hinders evolution of hydrogen chloride, thus contributing to the stabilization of the system, probably via an aromatic alkylation reaction. Preliminary kinetic analysis supports the idea that the mechanism of dehydrochlorination is of polaron type and yields values of the activation energy, calculated by method of Ozawa–Flynn–Wall (for $\alpha = 0.5$) in the range of 131.8–172.4 $kJmol^{-1}$. © 1997 Elsevier Science Ltd.

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Introduction

Thermogravimetric analysis (TGA) is one of the major thermal analysis techniques and has found a broad application in the field of characterization of polymeric materials[1–3]. For some studies, such as investigation of degradation mechanisms, it is however not sufficient since the thermoanalytical curves yield only a summarized information about the process, and cannot differentiate between partial reactions. Further information may be obtained from an analysis of first and subsequent derivatives, but it is essentially not possible to take a deeper look into the degradation mechanism. A valuable contribution is offered by a detailed kinetic analysis, with the first step of model-free determination of the activation energy.

A plethora of meaningful information is available on the thermal degradation/stabilization of polymers using hyphenated techniques, e.g. TGA coupled with Fourier transform infrared spectroscopy (TGA/FTi.r.). This technique provides continuous monitoring of the i.r. spectra of evolving volatile products in function of temperature with on-time measurement of sample's weight loss. It offers some advantages over other analytical techniques, like flash or direct pyrolysis—mass spectrometry (Py or DPy-MS) or thermal volatilization analysis (TVA), by making it possible to operate at modest, controlled temperatures and heating rates. This is crucial since at high temperatures organic polymers usually undergo complete thermal degradation and only low molecular weight fragments are obtained. In fact, in the mass spectrum of a polymer, the molecular ions of the thermal products will appear mixed with the fragment ions formed in the ionizing step[4]. This makes it difficult to deduce a degradation pathway. On the other hand, in the sealed tube the products of degradation are retained within a constant volume and may undergo secondary reactions while in a TGA experiment they are flushed out with the purge gas and the possibility of recombination is greatly reduced[5]. Again, this makes it difficult to infer a degradation route.

The drive to improve properties of poly(vinyl chloride) (PVC) has been underway for many years and has resulted in numerous papers[6–10]. In our laboratories we are dealing with novel class of thermal (secondary) stabilizers based on 9-(2,3-epoxypropane)carbazole (I). From our provious work[11,12] we can conclude that this class of compounds can exhibit the properties of a secondary stabilizer. Further research is focused on the investigation of influence of some derivatives of (I) on the thermal stability of PVC[13]. These substances have also proved to be efficient colourants for PVC.

Experimental

Materials. The samples were prepared by dilution of PVC-S [Zaklady Chemiczne Tarnów-Mościce S.A., molecular weight (M_n) = 46,000] with 3-(2,4-dichlorophenylazo)-9-(2,3-epoxypropane)carbazole in dimethylsulfoxide. The samples were then conditioned for 2 weeks under vacuum at 50°C to remove as much solvent as possible.

3-(2,4-Dichlorophenylazo)-9-(2,3-epoxypropane)carbazole was prepared by a coupling reaction of 9-(2,3-epoxypropane)carbazole, which was itself obtained as previously described in[12], with 3,4-dichlorophenyldiazo chloride[14]: to 3,4-dichloroaniline (0.36 g, 0.0022 mol) were added concentrated HCl (0.7 cm^3) and H_2O (3 cm^3). The mixture was carefully heated to 5–10°C and then cooled to 0°C. Then $NaNO_2$ (0.17 g, 0.025 mol) in H_2O (1.5 cm^3) was added at such a rate that the temperature did not exceed 5°C. After addition was complete, the reaction mixture was stirred for 20 min and subsequently neutralized to pH 6 by addition of NaOH. Next, 9-(2,3-epoxypropane)carbazole (0.5 g, 0.022 mol) in THF (10 cm^3) was added. The resulting mixture was stirred for 2 h at temp. 5°C and then for 4 h while the temperature was raised to the ambient temp. After evaporation of the solvent, the content was treated with CH_2Cl_2; the organic phase was washed with H_2O and the rest of the solvent was eliminated. 0.62 g of a homogeneous product (confirmed by h.p.l.c.) was obtained.

A description of the samples is given in *Table 1*.

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Table 1 Characteristics of the samples used in this work

Sample no.	Concentration (wt %) of additive in PVC	Additive
1	0 (pure PVC)	—
2	1	3-(2,4-dichlorophenylazo)-9-(2,3-epoxypropane)carbazole
3	5	3-(2,4-dichlorophenylazo)-9-(2,3-epoxypropane)carbazole
4	10	3-(2,4-dichlorophenylazo)-9-(2,3-epoxypropane)carbazole

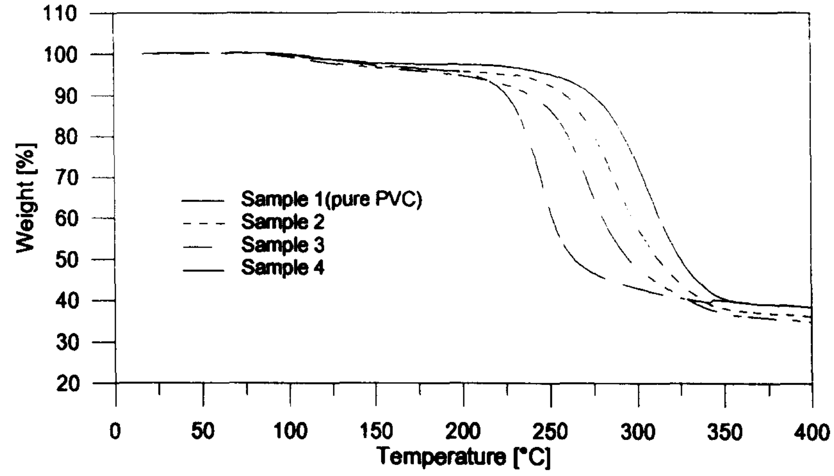


Figure 1 Thermogravimetric curves of samples 1, 2, 3 and 4 at 10 K/min^{-1}

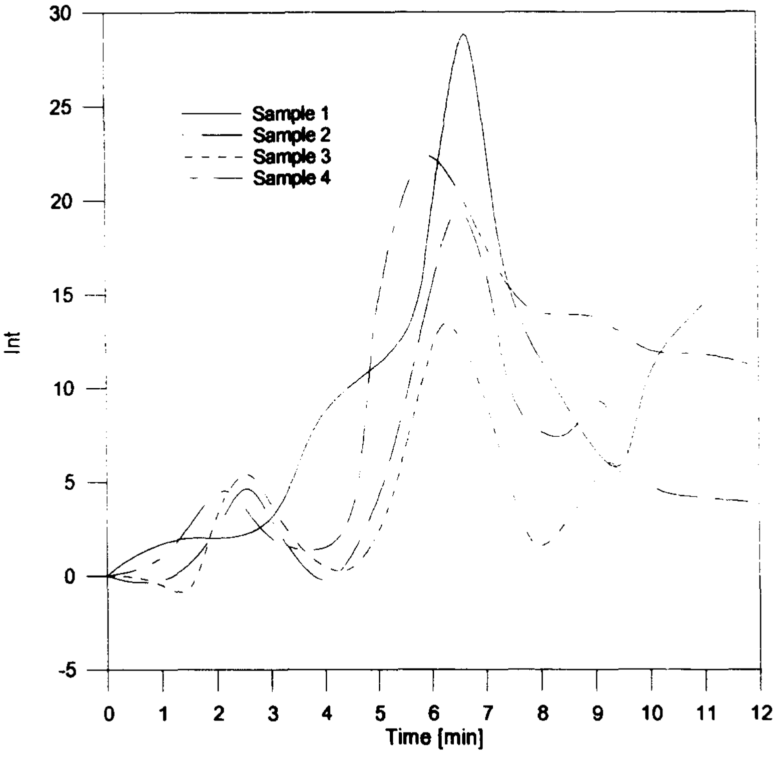


Figure 2 Gram–Schmidt chromatograms of samples 1, 2, 3 and 4

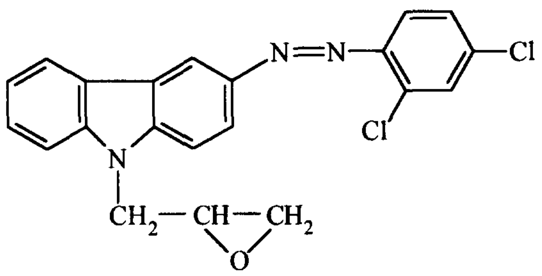
Techniques

Thermogravimetric analysis was carried out using a Perkin-Elmer 7 or a Shimadzu TGA-50 thermogravimetric analyser. The conditions were: heating rate = 2.5; 5; 10; 20 and 50 K/min^{-1}, sample weight ~5 mg, nitrogen flow = 50 cm^3/min. Fourier transform infrared (FT-i.r.) spectra were recorded using a Perkin-Elmer 1725X FT-i.r. spectrometer. The thermogravimetric analyser (P-E 7) and spectrometer were suitably coupled to enable the passage of evolved products from the furnace to the gas cell over a short path, to minimize secondary reaction or condensation on cell walls.

Spectrocolourimetric analysis was performed on an X-Rite 948 spectrocalorimeter operating in a reflection mode [$0^0/45^0$, D_{65} as iluminant, normal observer (2°)] with the results given in CIE (*x*, *y*, *z*) and Hunter (L, a, b) systems.

Results and discussion

From the chemical structure of additive under investigation, namely,



one can assume a twofold interaction with the PVC molecule. The first can be attributed to the glicydyl moiety which may confer a stabilizing action through the epoxy group; the second is connected with the steric hindrance afforded by the aryl structures.

Initially, analysis of the TG profiles shows that up to temperature of 200°C there is no substantial difference in the degradation route (*Figure 1*). The evolution of hydrogen chloride can be easily followed by an analysis of Gram-Schmidt chromatograms. It can be seen in *Figure 2* that the additive considerably diminishes the HCl emission profile.

The detection of HCl is very distinct with two characteristic aborption bands in the 2700–3050 cm^{-1} region.

The stabilizing effect can be explained by an aromatic alkylation reaction between the carbazole structure with the double bonds comprising the polyene sequences. The steric hindrance afforded by the aromatic molecule results in blocking access to the adjacent chlorine atoms and in influencing the polymer chain through electron interactions.

Some more explanation can be obtained on the basis of a kinetic analysis using the Ozawa–Flynn–Wall method[15,16]. Values of activation energy (apparent) are given in *Table 2*. Analysis of the results given in *Table 2* leads to the conclusion that the *E*-value of the degradation process of sample 2 (*Figure 3*) is higher than that of the other samples, respectively, and is also higher than that one of pure PVC.

In a general sense one can assume that the degradation route depends on the number of stabilizer molecules and can be explained by the fact that conjugation energy of the polyenyl cations formed in an ionic elimination reaches a limiting value for long sequences. The positive charge

Table 2 Calculated values of the activation energy from the Ozawa–Flynn–Wall analysis of the degradation process of samples 1–4 for $0.1 < \alpha_{\mathrm{global}} < 0.5$

	E (kJ/mol)			
α	Sample 1	Sample 2	Sample 3	Sample 4
0.1	132.5	164.6	133.2	121.5
0.2	137.1	163.2	133.4	126.9
0.3	139.1	166.8	133.7	127.2
0.4	139.7	167.7	134.8	128.2
0.5	140.0	172.4	133.9	131.8
0.6	142.1	174.8	134.0	137.6
0.7	144.8	178.1	137.0	148.8
0.8	149.1	188.9	141.6	171.9
0.9	157.3	206.7	158.7	190.4

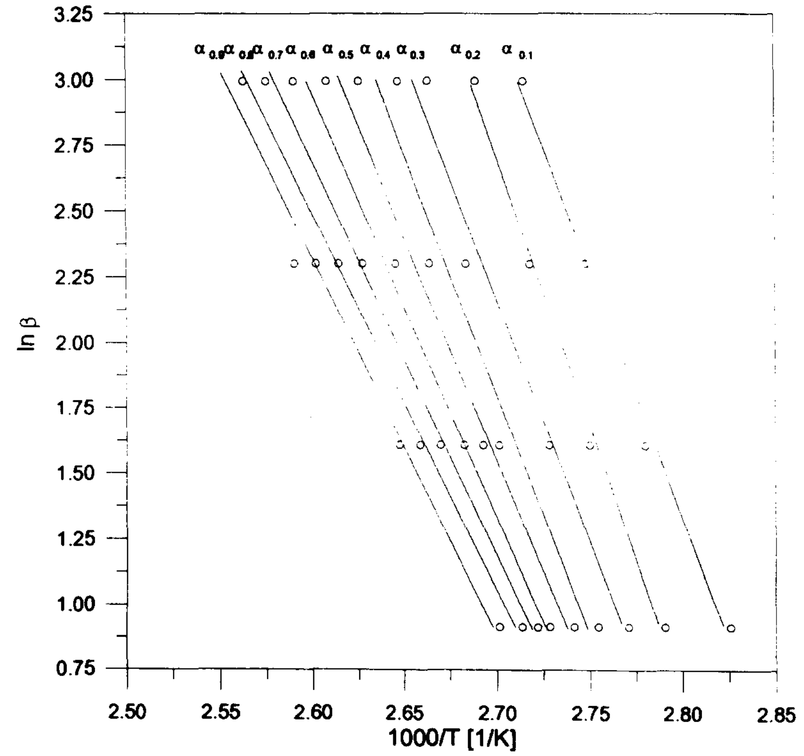


Figure 3 Ozawa–Flynn–Wall analysis of the degradation process of sample 2 for $0.1 < \alpha_{\mathrm{global}} < 0.5$

usually shows a strong tendency to be concentrated in the centre of the polyenyl cation. This will in turn decrease the ability of the chloride counterion to migrate to the sequence end in order to abstract a proton from the methylene group. Chloride counterion motion can be hindered by stabilizer's action via intermolecular forces. Both effects can be considered as important factors in restricting the length of the polyenes, thus limiting the amount of stabilizer needed.

Conclusions

3-(2,4-Dichlorophenylazo)-9-(2,3-epoxypropane)carbazole was succesfully used as a novel secondary stabilizer and colourant (data available upon request) for PVC. From the TG results it can be seen that this additive does not cause any significant decrease in the thermal stability of polymers up to 200°C. The reduction in HCl emission is a promising result for further studies with another, primary stabilizing system. An analysis of kinetic data in form of relationship α-E support the assumption that the process of dehydrochlorination is complex and presumably governed by a polaron mechanism.

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