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Short Communication

THERMAL STUDIES OF POLYVINYLCARBAZOLE AND POLYVINYLDIBROMOCARBAZOLE

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The thermal stabilities and behaviour of polyvinylcarbazole and polyvinyldibromocarbazole were investigated by a derivatograph. The initial and final temperatures of decomposition of these polymers were determined and their thermal properties compared.

Polyvinylcarbazole is one of the thermoplastic polymers characterized by considerable thermal stability. It is well known that the thermal stability of a polymer can be improved by attaching some additional atoms or functional groups to the chain. One of the successful methods is the attachment of a halogen atom. Morimoto and Mitsuda [1] have reported a method producing polyvinyldibromocarbazole by polymerizing vinyl 3,6-dibromocarbazole. This procedure, however, is difficult to carry out.

Some novel methods of obtaining polyvinyldibromocarbazole involve bromination of polyvinylcarbazole by means of a diluted bromate-bromide solution [2]. The reaction proceeds quantitatively, and bromine is attached to the 3 and 6 positions of the aromatic ring. Substitution of two bromine atoms in the carbazole ring should change its thermal behaviour markedly.

Experimental

Raw materials

Polyvinylcarbazole was obtained by polymerization of the monomer at room temperature in benzene solution with $AlCl_3$ as catalyst.

Polyvinyldibromocarbazole was obtained by bromination of polyvinylcarbazole in benzene by means of a bromate-bromide solution in the presence of 20% H_2SO_4 at room temperature [2]. The bromide content determined in the polymer (obtained by igniting and titrating as HBr) was 45.32% compared with a calculated value of 45.53%.

Apparatus and procedure

Experiments were carried out using a Paulik—Paulik—Erdey system Type OD 102 MOM derivatograph [3—5]. This instrument makes it possible to carry

out thermogravimetric (TG) and differential thermal analysis (DTA) simultaneously in a given temperature range. The studies were carried out in the range 20–600°, at an average heating rate of 5.8° per minute, with 0.250 g samples in a platinum crucible. Alumina, calcined at 1000°, was used as a reference material. All determinations were carried out in air.

Results

The results obtained by the study of polyvinylcarbazole (Fig. 1) show that its behaviour changes markedly on heating. Polyvinylcarbazole is practically stable up to about 300°, the DTA and TG curves not indicating any change. Above 300° an endothermic degradation begins, this degradation apparently involving the release of low molecular weight products. The degradation becomes exothermic in the range 390–450°.

The degradation process subsequently again becomes endothermic, as indicated by a DTA minimum at 460°. The polymer degradation is well observable on the

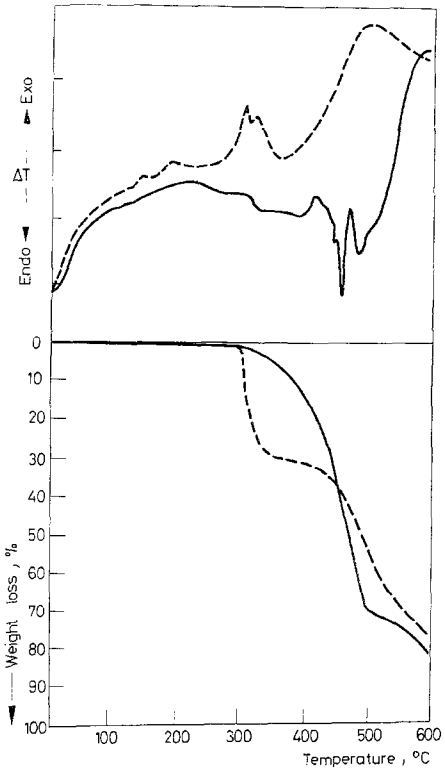

Fig. 1. TG and DTA curves of polyvinylcarbazole (——) and polyvinyldibromocarbazole (- - -)

TG curve, and the weight loss amounts to about 70% of the initial weight at about 500°. The product seems to remain stable up to about 520°. This behaviour can be interpreted by the fact that the endothermic degradation process is balanced by the exothermic oxidation. With further temperature increase some exothermic degradation of the polymer takes place, the degree of degradation amounting to 82 wt% at 600°.

Polyvinyldibromocarbazole behaves similarly to polyvinylcarbazole up to about 300°, and is stable in this temperature range. At 300° an exothermic degradation starts, the maximum on the DTA curve being at 310°. The TG curve, on the other hand, shows a very rapid loss of weight, amounting to 30 wt% at 350°. This behaviour is probably due to the splitting off of HBr from the polymer and to the uptake of oxygen, these processes balancing in the range 350–420° where the loss of weight is as little as 3 wt%. Above 420°, a progressive exothermic degradation of the polymer occurs, the weight loss amounting to 77 wt% at 600°. Polyvinylcarbazole and polyvinyldibromocarbazole are thermally resistant up to about 250°.

References

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