Thermochimica Acta, 9 (1974) 79–80

Note

Thermogravimetry of some copolymers

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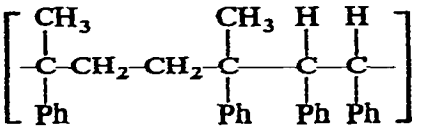
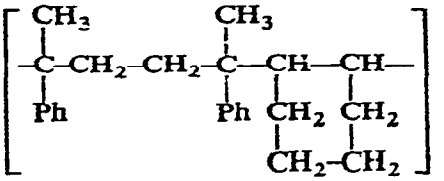
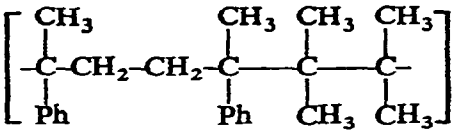
(Received 19 October 1973)

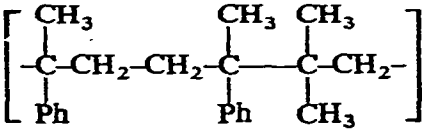
In order to produce more thermally stable materials it is desirable to be able to relate stability and chemical structure. Some guides in this direction have already been defined. For example it is now accepted that crosslinking increases stability. The development of a technique[1] for synthesising polymers of controlled chemical structure makes it possible to study systematically the relationship between chemical composition and thermal decomposition characteristics. In this note we wish to show some data which illustrate clearly the importance of steric effects on the thermal stability of a series of copolymers.

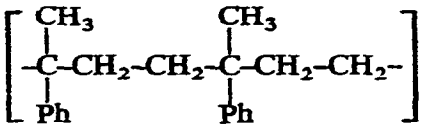
The copolymers were produced using the Richard's synthesis[1], and had the following structures:

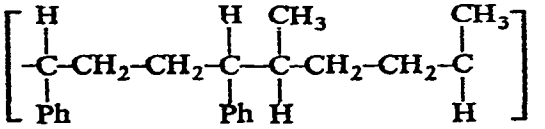
(1) 

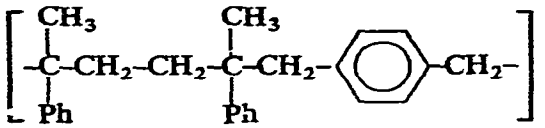
(2) 

(3) 

(4) 

(5) 

(6) 

(7) 

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The compositions of the copolymers were checked using NMR.

The thermogravimetry of the copolymers was carried out using a Stanton massflow thermobalance. The samples were in vacuo and heated at 3 °C min^{-1}. The results are shown in Fig. 1.

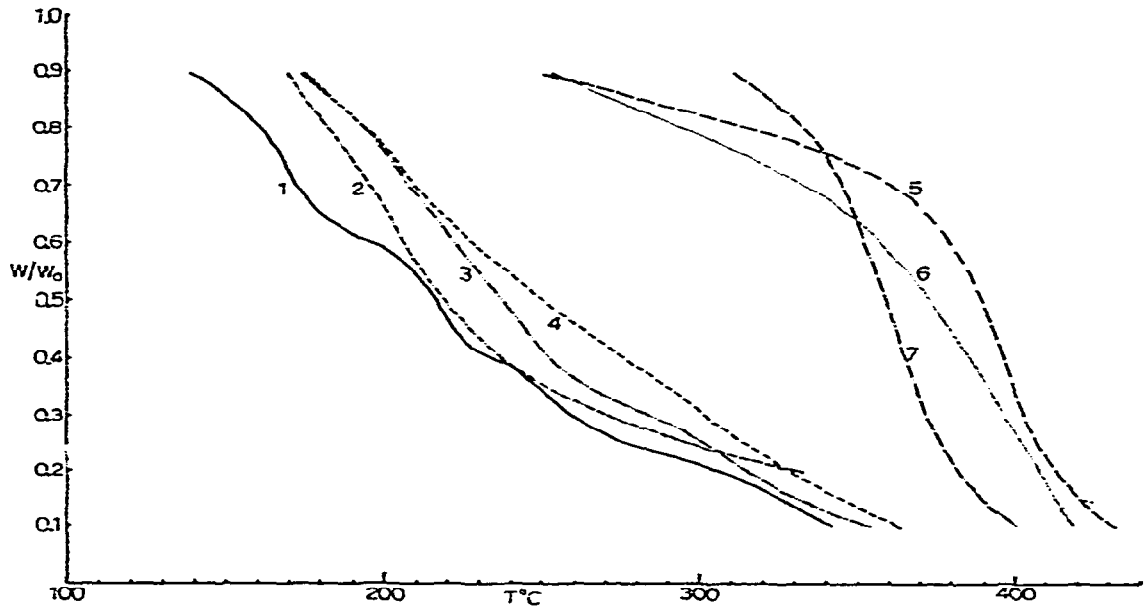

Fig. 1. Fractional conversion versus temperature for a series of copolymers heated at 3°C min^{-1}.

There is a very marked difference in stability between copolymers 1–4, and copolymers 5–7. Sample 1 which has the highest proportion of benzylic bonds in the main chain is very unstable, and 2–4 scarcely show any improvement. On the other hand samples 5–7 show the behaviour of the more typical organic polymers. On examining the chemical structure of the copolymers it can be seen that copolymers 1–4 show considerable steric crowding along the main chain. This is more evident when molecular models are compared with those for 5–7, which have much less crowding.

Thus the conclusion of the study of the thermogravimetry of this series of copolymers is that steric strain plays a very important role in initiating thermal decomposition.

REFERENCE

1 D. H. Richards, N. F. Scilly and F. J. Williams, *Chem. Commun.*, (1968) 1285.