

the radius of gyration of the molecule in the crystalline state has been calculated from the crystallographic atomic co-ordinates, a more quantitative comparison will be possible.

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Competition between Scission and Cross-linking Processes in the Thermal Degradation of a Polycarbonate

WE have previously reported¹ that, when poly(2,2-propanebis(4-phenyl carbonate)) is heated in a sealed evacuated tube, random scission of the polymer occurs without gel formation. We have now found that the polymer is rapidly cross-linked to form a gel if the volatile products are continuously removed (10^{-3} mm vacuum) during the degradation.

The gel content of the material after heating at a constant temperature was determined by extraction of the degraded polymer with methylene chloride, the sol content by evaporation of a portion of the extract. The intrinsic viscosity of the sol fraction in methylene chloride was determined by dilution viscometry.

Fig. 1 shows the gel content of the degraded polymer as a function of time of heating at 323°C; the gel point occurred at 0.5 h. The viscosity results (Fig. 2) show that the intrinsic viscosity of the polymer and, after the gel point, of the sol fraction increases with time of heating to a maximum value (after 1.2 h at 323°C) and thereafter decreases. For comparison the viscosity changes of the polycarbonate heated in a sealed tube at approximately the same temperature (331°C) are also included in Fig. 2. It can be seen that in the latter case the polymer undergoes a continuous decrease in viscosity.

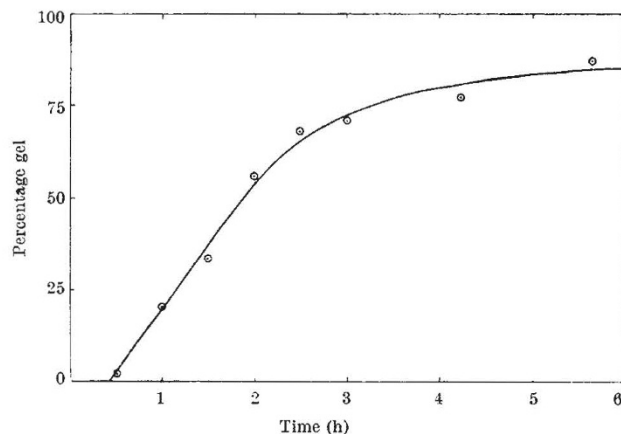


Fig. 1. Gel-formation (per cent) in polycarbonate heated in a continuously evacuated system versus time (h) at 323°C

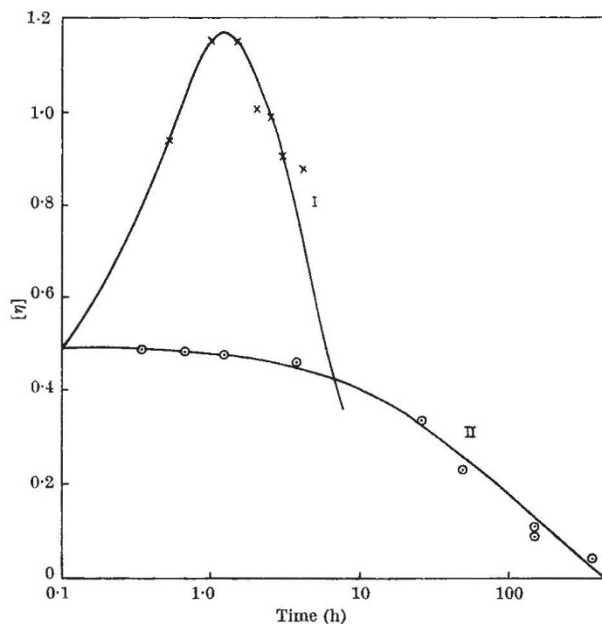


Fig. 2. Change in intrinsic viscosity $[\eta]$ of sol fraction of polycarbonate specimens with time of heating: I, continuously evacuated system at 323°C, gel point at 0.5 h; II, sealed evacuated system at 331°C, no gel formed

It is apparent from Fig. 2 that the gel point does not coincide with the time required to reach the maximum viscosity as predicted by the network theory of Flory². In the present case the divergence is probably due to further condensation of the polymer on heating which is consistent with the observed evolution of bisphenol A during the reaction.

The results obtained show that the thermal degradation of the polycarbonate involves a finely balanced competition between scission and cross-linking processes. The mode of degradation which predominates depends solely on whether or not certain volatile products, probably phenols, are removed from the degrading polymer. Earlier reports³⁻⁵ of gel-formation under various conditions of degradation can thus be readily explained.

The present results stress the dependence of the physical nature and properties of a polymer on the degradation conditions as it is apparent that a slight alteration in these conditions can drastically change the overall mechanism of breakdown.

A more detailed investigation of the thermal behaviour of polycarbonate is at present under way.

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BIOPHYSICS

Ontogeny of Biological Order

THE sequence of nucleotides in polydeoxyribonucleic acid (DNA) has been established as the principal molecular determinant of heredity. Ontogeny is believed to reflect temporal patterns of DNA transcription^{1,2}. By participation in the flow of genetic information from DNA to poly-