

ciently large to be detectable by simple viscometric methods in current use. These methods are capable of giving viscosity-average molecular weights to an accuracy of at least 1 per cent. Moreover, Hermans and Kooy<sup>5</sup> have described apparatus with which limiting viscosity numbers may be determined with a precision of better than 0.1 per cent. The proposed method is therefore directly applicable within the limits of precision at present attainable, and has the advantage of requiring only one technique of measurement. In addition, measurements of  $\bar{M}_{vA}/\bar{M}_{vB}$  may be made comparatively quickly and only small quantities of polymer are necessary. The accuracy of the method will be affected less by errors in the absolute values of the constants of the Houwink equations for the two solvents than by errors in their relative magnitudes. Since values of these constants in different solvents are often obtained by viscometric determinations on the same polymer samples, little error should arise when constants derived in this way are used.

P. F. ONYON

Department of Chemistry,  
College of Technology,  
Birmingham.  
Feb. 25.

<sup>1</sup> Tompa, H., "Polymer Solutions" (Butterworths Sci. Pub., London 1956).

<sup>2</sup> Bamford, C. H., Barb, W. G., Jenkins, A. D., and Onyon, P. F., "Kinetics of Vinyl Polymerization" (Butterworths Sci. Pub., London, 1958).

<sup>3</sup> Schulz, G. V., *Z. phys. Chem.*, B, **43**, 25 (1939).

<sup>4</sup> Zimm, B. H., *J. Chem. Phys.*, **16**, 1099 (1948).

<sup>5</sup> Hermans, J. J., and Kooy, J., *J. Polymer Sci.*, **16**, 417 (1955).

### Direct Examination of the Degradation of High Polymers by Gas Chromatography

EXAMINATION of the degradation products of high polymers may give an indication of the mechanism of breakdown, and may also yield information about the structure and composition of polymers and copolymers. Such an examination may be quickly and conveniently effected if the degradation products are characterized by gas chromatography as they are formed. This may be achieved by generating a pulse of degradation products in the chromatographic apparatus, which is so designed that the products are swept into the column with the minimum delay and disturbance.

Two degradation techniques have been applied in this way. In the first method, a few milligrams of polymer sample are used as a dielectric which is broken down by triggering through it a high-energy discharge (up to 2,000 joules). This method has been applied to polyethylene, polyvinyl alcohol, polyvinyl acetate, polyvinyl chloride, polymethyl methacrylate, polystyrene and cellulose acetate. In all cases the degradation is very drastic, the principal products being small unsaturated molecules with acetylene in largest yield. In some cases (for example, polystyrene), 'characteristic' fragments (for example, toluene, styrene,  $\alpha$ -methyl styrene) are also obtained; but the yield of these in comparison with the small unsaturated molecules cannot be significantly increased by variation of the experimental parameters. Hence this method is of only limited utility for structure determination, and the secondary thermal effects are so predominant that no information about the mechanism of the primary electrical breakdown is derived.

The second technique may be controlled to give any desired degree of thermal degradation, and has proved to be more versatile in application. The method involves coating or placing the polymer sample on a filament, which can quickly be brought to any specified temperature for a brief period. The temperature calibration of the filament is effected by optical pyrometry and also by melting-point observations. Samples up to several milligrams have been examined, and the sensitivity of the gas chromatography apparatus is such that less than 1  $\mu$ gm. of a component in the degradation products may be detected.

Two principal applications of this second degradative technique are under investigation. The first is in the rapid estimation of copolymer composition. The procedure here is simply to degrade the copolymer sample at a particular temperature and to measure peaks on the chromatogram characteristic of each constituent of the copolymer; for example, for vinyl chloride-vinyl acetate copolymers the hydrogen chloride and acetic acid peaks have been used. Separate experiments on weighed samples of the pure homopolymers have yielded direct relations between their masses and the sizes of the characteristic peaks, and these relations enable the sizes of the peaks in the copolymer chromatogram to be translated into masses of the two monomers present. In Table 1 the results obtained for three vinyl chloride-vinyl acetate copolymers are compared with those obtained by infra-red analysis.

Table 1. PERCENTAGE VINYL ACETATE IN VINYL CHLORIDE-VINYL ACETATE COPOLYMERS

By infra-red analysis	By degradation
26.7 $\pm$ 1.0	26.2 $\pm$ 0.8
34.6 $\pm$ 1.0	31.4 $\pm$ 0.7
44.3 $\pm$ 1.0	43.9 $\pm$ 0.5

The second application of the technique consists of recording the degradation products from the same sample of polymer maintained for a few seconds at each of a series of temperatures up to 1,000° C. Polystyrene, polyvinyl chloride, polyvinyl acetate and polymethyl methacrylate have been examined in this way, and each polymer gives a characteristic 'spectrum'. (Under the conditions used, the whole temperature-range can be covered in less than half an hour, and the results give a rapid identification of unknown polymers.) The relative proportions of the degradation products at each temperature yield information about the relative importance of the various degradation processes throughout the temperature-range. For example, it can be shown in the case of polyvinyl acetate that simple depolymerization is a relatively insignificant process; that loss of acetic acid is the principal degradation process and occurs at intermediate temperatures, and that the resulting polyacetylene skeleton is much more stable and is degraded principally at the highest temperatures.

This procedure is also being applied to copolymer samples, and a method of distinguishing block from random copolymers is projected.

Full details of this work and of the modifications in hand will shortly be published elsewhere.

R. S. LEHRLE  
J. C. ROBB

The Chemistry Department,  
The University,  
Edgbaston,  
Birmingham, 15.