

CHROM. 4125

A MODIFIED METHOD FOR THE ANALYSIS OF OXYETHYLENE/ OXYPROPYLENE COPOLYMERS BY CHEMICAL FISSION AND GAS CHROMATOGRAPHY

J. B. STEAD AND A. H. HINDLEY

Analytical Research Department, Lankro Chemicals Ltd., Eccles, Manchester (Great Britain)

(First received March 10th, 1969; revised manuscript received April 11th, 1969)

SUMMARY

A modification of the MATHIAS-MELLOR HBr fission/GLC method for determining the oxyethylene content of polyoxyethylene-polyoxypropylene copolymers is described, which eliminates arbitrary correction factors. The results are independent of molecular weight and oxyalkylene distribution of the materials and are within the limits of variation of commercial products, *i.e.*, $\pm 1\%$ at 50% oxyethylene and $\pm 0.1\%$ at 3%. The reproducibility of replicate determination is normally better than this. Some of the disadvantages of infrared methods are also discussed.

INTRODUCTION

Copolymers of ethylene and 1,2-propylene oxides are widely used in the surfactant and polyurethane industries. Materials having up to 80% by weight of oxypropylene sandwiched as a block between two oxyethylene blocks are valuable non-toxic surfactants^{1,2}, and diol or triol based copolymers containing 0-15% oxyethylene arranged either randomly or in a variety of blocked distributions³ are used to make urethane foams by reaction with isocyanates. An accurate knowledge of the oxyethylene content is desirable for plant control of these materials since small variations can cause major problems, particularly in urethane foam formation, and recently analytical methods using infrared (I.R.)⁴ and nuclear magnetic resonance (N.M.R.) spectroscopy⁵ have been described. Since all spectrometric methods measure only the oxypropylene methyl group signals they are least suitable for urethane polyethers containing only small amounts of oxyethylene, and I.R. methods in particular have additional disadvantages discussed later.

MATHIAS AND MELLOR⁵ used controlled fission of the copolymer with HBr-acetic acid reagent to give ethylene and 1,2-propylene dibromides which were determined by gas chromatography. Propylene dibromide was less stable than ethylene dibromide under the fission conditions and arbitrary factors were necessary to account for its preferential removal. Our experiments with the method showed that these factors were too dependent on variations in reaction conditions, although these were

controlled as rigidly as possible, to permit results to better than $\pm 2-3\%$ oxyethylene at the 50% level and $\pm 1-2\%$ at the 10% level. However, by modifying the conditions and using weighed mixtures of miscible polyoxyethylene and polyoxypropylene glycols as bracketing standards we were able to dispense with these factors. The basic assumption, which has been amply justified in practice, is that any variations in reaction conditions are compensated for by subjecting both samples and standards to the same treatment. The modified method, described below, has been adopted for routine use in this laboratory.

EXPERIMENTAL

Gas-liquid chromatographic apparatus and conditions

A Pye Model 104 gas chromatograph (Pye Unicam Limited, Cambridge, Great Britain) equipped with a flame ionisation detector, was used. The column was a 9 ft. \times $\frac{1}{4}$ in. I.D. glass column containing 10% Apiezon L on 80-100 mesh Chromosorb W, operated isothermally at 125°. The prepared packing material was obtained from Varian Aerograph, Fife, Great Britain. The carrier gas (nitrogen) flow was 40 ml/min. The GLC conditions are not critical and any conditions giving well separated peaks for ethylene and propylene dibromides, will suffice.

Reagents and standards

45% w/v hydrogen bromide in glacial acetic acid (British Drug Houses Ltd., Poole, Dorset, Great Britain) was used for the chemical fission. This was obtained in 100 ml sealed ampoules and in order to avoid deterioration from atmospheric moisture was immediately transferred on opening to a number of small ampoules (3-5 ml), one of which was used for each test.

The standards used were weighed mixtures of the two miscible homopolymers, polyoxyethylene glycol mol. wt. 414 and polyoxypropylene glycol mol. wt. 540. These materials, from now on referred to as PEG 414 and PPG 540 respectively, were made by reacting the alkylene oxides with ethylene glycol or 1,2-propanediol as appropriate, using a potassium hydroxide catalyst.

AnalaR grade carbon disulphide was used for extracting the dibromides.

METHOD

A mark was made with a glass file on a length of capillary melting point tubing at a position such that when broken off, the small piece contained $20 \pm 2 \mu\text{l}$ of liquid. The tube was filled past the mark with the sample and wiped externally with paper tissue. It was then broken and the portion containing the sample dropped into a thick walled Pyrex glass tube (100 \times 8 mm I.D. with walls 2 mm thick), sealed at one end. Similar marks were made by measuring on three more melting point tubes taken from the same batch and three further reaction tubes prepared containing a duplicate sample and two standards. The latter were weighed mixtures of PEG 414 and PPG 540 such that one contained about 2% more oxyethylene than expected in the sample and the other about 2% less. To each tube 0.4 ml of the HBr/acetic acid reagent was added by means of a 1 ml graduated pipette, and the tubes were sealed in a small, hot flame. They were then placed in a shallow beaker in a forced draught oven

at $150 \pm 1^\circ$ for 3 h, then removed, allowed to cool for 20 min, and opened. The contents of each tube were washed into a test tube (100×10 mm) fitted with a glass stopper, using 4 ml of water measured from a 5 ml measuring cylinder to effect complete transfer. Carbon disulphide (1.5 ml) was added to each tube which was stoppered, shaken vigorously for 1 min, then set down for the layers to separate.

A $0.5 \mu\text{l}$ sample of the lower layer from each test tube was injected into the gas chromatograph and the areas of the ethylene dibromide (EBr_2) and propylene dibromide (PBr_2) peaks in the chromatograms measured. The area ratio (A)

$$A = \frac{\text{EBr}_2 \text{ peak area}}{\text{EBr}_2 \text{ peak} + \text{PBr}_2 \text{ peak area}}$$

was obtained in each case and the mole fraction (X) of oxyethylene in the oxyalkylene chain calculated for the sample duplicates from each standard as follows

$$X = \frac{X_0 \cdot A}{A_0}$$

where X_0 is the mole fraction of oxyethylene in the standard and A and A_0 the area ratios obtained for the sample and standard respectively. The average of the four values of X thus obtained was taken as the result for the sample. The weight percentage of oxyethylene was calculated thus

$$\text{wt. \% E.O.} = \frac{75.9 X}{1 - 0.242 X}$$

Notes

(1) A linear variation of A with X is assumed in the calculation. Although this is not strictly correct (see Fig. 1), the deviations can be neglected provided that the composition of the standards and samples does not differ greatly.

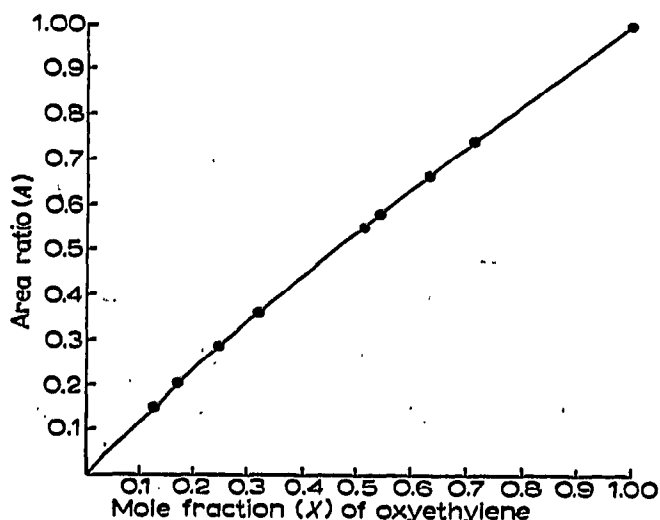


Fig. 1. Variation of area ratio (A) with mole fraction (X) for PEG 414/PPG 540 standards.

(2) The reaction time is 3 h rather than the 2 h used by MATHIAS AND MELLOR. This increased time led to better agreement between the values of A from duplicate samples, and no signs of products of incomplete bromination were observed in the chromatograms. Additional minor peaks were usually present when a 2 h reaction time was used. Although the degradation of propylene dibromide relative to that of ethylene dibromide is increased by the extended period, the effect is assumed to be the same for both samples and standards. This assumption is justified by the results obtained (Table I).

(3) For washing the reaction tubes 4 ml of water are used rather than the 0.7 ml used by MATHIAS AND MELLOR, since the larger volume facilitates complete transference of the fission products into the test tubes. The extraction of the dibromides into the organic phase is possibly less efficient but, being the same for the standards, is unimportant.

TABLE I
TYPICAL GLC RESULTS FOR VARIOUS COPOLYMERS

Sample	Initiator	Oxyalkylene distribution (E = oxyethylene) (P = oxypropylene)	Mol. wt.	% E.O. theory	% E.O. found
1	<i>n</i> -butanol	E + P	1,500	51-52	51.7, 51.9, 52.2
2	<i>n</i> -butanol	random	1,500	51-52	51.8, 52.2
3	glycerol	random	5,800	51-52	50.8, 51.2
4	<i>n</i> -butanol	P + E	1,500	51-52	51.7, 51.8
5	<i>n</i> -butanol	E + P + E + P	1,500	51-52	51.3, 51.2
6	<i>n</i> -butanol	P + E + P + E	1,500	51-52	51.4, 51.3
7	<i>n</i> -butanol	random	650	42	42.0, 42.2
8	<i>n</i> -butanol	random	1,750	42	42.7, 43.0
9	<i>n</i> -butanol	random	3,000	42	42.3, 42.0
10	<i>n</i> -butanol	random	3,000	48	47.6, 47.2
11	ethylene glycol	random	3,700	50	49.4, 49.6
12	water	random	3,800	25	24.8, 24.8
13	water	random	5,600	30	29.3, 29.0
14	water	random	1,200	60	59.5, 58.8
15	water	random	3,800	75	75.0, 74.5
16	glycerol	P + E	4,800	10	9.7, 9.6
17	glycerol	P + E	3,500	3	2.9, 2.9

RESULTS AND DISCUSSION

Fig. 1 shows the variation of area ratio (A) with mole fraction (X) of oxyethylene for a series of PEG 414/PPG 540 mixtures, and the results obtained for some typical copolymers having a variety of initiating bases, molecular weights, and oxyalkylene distributions are given in Table I. It is clear that the results are independent of these factors, indicating that the reagent attacks at all ether linkages indiscriminately rather than by degradation from the end of the chain. In a further experiment to examine the effect of molecular weight variations a random copolymer was made by reacting glycerol continuously with a mixture of equal weights of ethylene and

propylene oxides. Samples taken when the molecular weight of the product was 350 and 5,400 gave identical area ratios (A) in duplicate tests to within $\pm 0.5\%$.

Experiments to examine the effect of moisture in the samples showed that up to 0.2% of water had no observable effect. The results for many copolymers made on a carefully controlled weight basis were always within $\pm 1\%$ of the theory at the 50% oxyethylene level and within $\pm 0.1\%$ at the 3% level. The reproducibility of replicate determinations was in most cases considerably better than this but higher accuracy cannot be claimed owing to the difficulty of making standard copolymers to finer limits.

Prior to adopting the HBr fission method for the routine control of production copolymers we investigated regular and overtone I.R. spectroscopic methods differing only in minor respects from those recently described by WEIS⁴. These depend on measuring the ratio of absorbances due to CH_3 and OCH_2 groups (7.27μ and 7.4μ respectively) in the regular I.R. and to CH_3 and CH_2 groups (1.17μ and 1.20μ) in the overtone region. The oxyethylene content is obtained in both cases from a calibration graph prepared using standard copolymers, mixtures of polyoxyethylene and polyoxypropylene glycols being used in the published method. Our results showed that the band intensities varied with molecular weight and oxyalkylene distribution in copolymers with the same oxyethylene content, particularly with the regular I.R. method, and Table II shows the absorbances observed for the first three copolymers of Table I, examined as 2.00% w/v carbon tetrachloride solutions in a 0.400 mm path length cell.

TABLE II

I.R. BAND INTENSITIES IN COPOLYMERS CONTAINING 51-52% OXYETHYLENE

Sample	Oxyalkylene distribution	Mol. wt.	7.27μ (CH_3) absorbance (± 0.002)	7.41μ (OCH_2) absorbance (± 0.002)
1	E + P	1,500	0.264	0.150
2	random	1,500	0.273	0.131
3	random	5,800	0.276	0.085

The ratio of absorbances is particularly sensitive to small differences in molecular structure since the oxyalkylene distribution affects the two bands in opposite senses. The overtone method shows less variation with distribution but is still very susceptible to differences in molecular weight.

The I.R. methods have the advantage of rapidity over the fission method and in our experience are useful for the routine testing of copolymers containing more than 20% oxyethylene, provided that the standards used have the same structure and molecular weight as the samples. They fail completely, however, for materials containing less than 15% oxyethylene such as those used in urethane foam manufacture. The modified fission method is particularly suitable for these materials since characteristic chromatogram peaks are obtained from both oxyethylene and oxypropylene groups. Thus it is more reliable than the N.M.R. method⁵ at the 0-5% oxyethylene level, and the necessary equipment is, incidentally, much less expensive. An added advantage

is that base initiators can be identified by increasing the temperature of the gas chromatographic column, as has been shown by MATHIAS AND MELLOR⁵.

ACKNOWLEDGEMENTS

The authors thank the Directors of Lankro Chemicals Ltd. for permission to publish this work, in particular the Research Director, Mr. A. J. LOWE for valuable suggestions and criticism. Also Dr. R. DYKE of the Polyether Research Department, Lankro Chemicals Ltd. for supplying the standard copolymers, and Drs. G. ROSSMY and A. BRUSDEYLINS of Th. Goldschmidt A.G., Essen, G.F.R., for inter-laboratory evaluation of the method.

REFERENCES

- 1 T. H. VAUGHN, H. R. SUTER, L. G. LUNSTED AND M. G. KRAMER, *J. Am. Oil Chemists' Soc.*, 28 (1951) 294.
- 2 I. R. SCHMOLKA, *Am. Perfumer Cosmet.*, 82 (1967) 25.
- 3 A. J. LOWE, E. F. CHANDLEY, H. W. LEIGH AND L. MOLINARIO, *J. Cellular Plastics*, 1 (1965) 121.
- 4 G. WEIS, *Fette, Seifen, Anstrichmittel*, 70 (1968) 355.
- 5 A. MATHIAS AND N. MELLOR, *Anal. Chem.*, 38 (1966) 472.

J. Chromatog., 42 (1969) 470-475