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Gas-liquid chromatographic separation of ethyl acrylate and methyl methacrylate

Several methods are available for the study of the copolymerisation behaviour of a mixture of monomers, based either on the analysis of the copolymer composition, or on the determination of the residual monomer content.

By the addition of inhibitors in different reaction steps, copolymerisation may be stopped; the polymer is then isolated and analysed by different techniques: IR spectroscopy, chemical analysis, etc.¹⁻⁴. Direct residual monomer analysis could avoid time-consuming precipitation and isolation steps based on the polymer^{5,6}.

Since the physical and chemical properties of the two above-mentioned monomers are similar, the analytical method has to be very selective. Polarography, chemical analysis (*e.g.* mercaptan addition) etc.⁷ will give the total amount of monomers, while gas chromatography will allow the separation and the quantitative determination of the two monomers.

The most common phases used for the separation of ethyl acrylate and methyl methacrylate are a high vacuum grease^{8,9} or a silicone oil¹⁷ for packed columns and polypropylene glycol (PPG) for capillary columns¹⁰.

First trials in our laboratory gave a partial separation on several stationary phases (Table I), but it was not possible to obtain good quantitative analysis as the concentration ratio of the monomers will vary from 95/5 to 5/95.

The two monomers are best separated on PPG 400 but the separation obtained is not enough for accurate quantitative analysis. As in earlier experiments¹¹, selectivity properties of the organo-clay Bentone 34 were checked, and by using equal amounts of stationary phase and Bentone 34, the relative retention volumes became 3.60 for ethyl acrylate, 3.90 for methyl methacrylate and 5.25 for water.

After some trials, it was found that water retention time was decreasing quickly whilst ethyl acrylate-methyl methacrylate separation remained unchanged. To avoid

TABLE I

RETENTION VOLUMES OF ETHYL ACRYLATE AND METHYL METHACRYLATE ON VARIOUS STATIONARY PHASES

Stationary phase ^a	Column temperature (°C)	Relative retention volumes ^b		
		Ethyl acrylate	Methyl methacrylate	Water
PEG 200	70	2.44	2.55	> 30
PEG 600	85	2.02	2.13	> 20
PPG 400				
PPG 400	60	2.95	3.21	3.75
Tetraethylene glycol dimethyl ether	60	4.55	4.70	5.80
Silicone oil	60	6.02	6.35	5.00

^a 30 parts of stationary phases are poured on to 70 parts of Chromosorb P, 60-80 mesh; the columns are made of copper tube 2-m long and 4 mm I.D.

^b Retention volumes are measured by comparing with that for acetone.

any interference from the water peak, it is necessary to use a water-retardant stationary phase: diglycerol or polyethylene glycol 200.

Experimental

From HETP determinations, optimum flow rate and temperature were checked and the following experimental conditions were used:

Chromatograph: Perkin-Elmer 116 with a thermistor detector.

Columns: Precolumn, copper tube, length 0.3 m, I.D. 4 mm; 30 % PEG 200 on Chromosorb P, 60-80 mesh. Analytical column, copper tube, length 4 m, I.D. 4 mm; 5 % PPG + 5 % Bentone 34 on Chromosorb P 60-80 mesh.

Temperature: Columns and detector: $60^{\circ} \pm 0.1^{\circ}$; injector 100° .

Carrier gas: Hydrogen (flow rate 40 ml/min).

Sample: 10 μ l.

Recorder: Philips PR 1040, 2 mV.

Retention volumes, corrected for dead volume, were measured and compared with that for acetone (Table II).

TABLE II

RELATIVE RETENTION VOLUMES AND KOVATS INDICES OF VARIOUS COMPOUNDS ON BENTONE 34/PPG 400

Compounds	Relative retention volumes	KOVATS indexes
Acetone	1.00	not determined
Methanol	not determined	772
Ethanol	2.07	810
Ethyl acrylate	2.89	848
Methyl methacrylate	3.33	863

For quantitative analysis, the external standard addition method was chosen, with acetone as reference compound. Acetone is soluble in organic and aqueous media and does not precipitate the emulsions. Standardisation was carried out with artificial emulsions and solutions containing 0.2-20 % of ethyl acrylate and/or methyl methacrylate. Statistical analysis gives a reproducibility of 3 % (relative value). At concentrations below 0.2 %, monomers cannot be determined by the above method, because of the lack of detector sensitivity and the high viscosity of emulsions.

Different methods were considered: (1) the use of a high-sensitivity detector after dissolving the emulsion in a suitable solvent^{12,13}; (2) the use of the same chromatographic conditions, as above, after a concentration step of the residual monomers by extractive distillation¹⁴.

Benzene was chosen as extractive solvent; the distillation apparatus consisted of a 500-ml boiler, an azeotropic distillation receiver and a condenser, all connected with ground-glass joints.

5 g of benzene were added to 100 g of the acrylic emulsion; after some minutes of vigorous agitation, the mixture was refluxed for 30 min in the distillation apparatus. Then, all the organic phase was in the azeotropic distillation receiver with a small amount of water. The aqueous phase was discarded and the organic layer analysed

by gas chromatography under the experimental conditions described above. Benzene, ethyl acrylate and methyl methacrylate were successively eluted.

Quantitative analysis was based on area normalisation, each peak area being multiplied by the corresponding correction factor which was determined from artificial standard mixtures of monomers and solvent. The reproducibility between 100 and 1000 p.p.m. of each monomer was about 5 % for ethyl acrylate and 10 % for methyl methacrylate.

Pyrolysis techniques used in conjunction with gas chromatography are now a very useful tool for elucidating the composition of macromolecules and have been reviewed^{15,16}.

By use of the GC separation described above and the choice of optimum conditions of pyrolysis, it was easy to obtain characteristic pyrograms of the acrylic polymers and copolymers. Polymethyl methacrylate yields only the monomer peak whilst the polyethyl acrylate pyrogram shows two main peaks: ethanol and ethyl acrylate.

The most reproducible pyrograms were obtained with a Curie-point apparatus (Philips PW 4080) but quantitative analysis was unsuccessful: some unknown parameters were affecting the pyrolytic degradation reaction, as we have already pointed out⁴; the pyrograms are quantitatively different for true statistical copolymers (generally obtained at low monomer conversion) and with industrial copolymers (obtained with a high degree of conversion). For example, in the ethyl acetate-methyl methacrylate copolymer pyrograms, the ratio between the peak heights of ethyl acrylate and ethanol is 3.65 for a statistical copolymer and about 0.80 for a factory-made copolymer of the same chemical composition.

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- 1 M. FIGEYS, personal communication, 1963.
- 2 J. HASLAM AND H. A. WILLIS, *Identification and Analysis of Plastics*, London Iliffe Books, London, 1965.
- 3 J. HASLAM, J. B. HAMILTON AND A. R. JEFFS, *Analyst*, 83 (1958) 63.
- 4 A. ALLOING AND J. DANDOY, *XXXVIème Congr. Intern. Chim. Ind. Bruxelles, Sept. 1966, Ind. Chim. Belge*, 32 (1967) 182.
- 5 A. GUYOT AND J. GUILLOT, *J. Chim. Phys.*, 61 (1964) 1434.
- 6 J. DANDOY AND C. DENEUBOURG, personal communication, 1968.
- 7 G. M. KLINE, *Analytical Chemistry of Polymers*, Vol. XII, Part I, International Publishers, New York, 1959.
- 8 R. L. GATRELL AND T. J. MAO, *Anal. Chem.*, 37 (1965) 1294.
- 9 J. J. CINCOTTA AND R. FEILAND, *Anal. Chem.*, 36 (1964) 488.
- 10 C. W. STANLEY AND W. R. PETERSON, *SPE Trans.*, 2 (1962) 298.
- 11 J. DANDOY, *J. Chromatogr.*, 32 (1968) 184.
- 12 P. SHAPPRAS AND G. C. CLAVER, *Anal. Chem.*, 36 (1964) 2282.
- 13 L. B. WILKINSON, C. W. NORMAN AND J. P. BUETTNER, *Anal. Chem.*, 36 (1964) 1759.
- 14 O. TWEET AND W. K. MILLER, *Anal. Chem.*, 35 (1963) 852.
- 15 G. M. BRAVER, *J. Polym. Sci., C*, (1965) 3.
- 16 M. BEROZA AND R. A. COAD, *J. Gas Chromatogr.*, 4 (1966) 199.
- 17 H. McCORMICK, *J. Chromatogr.*, 40 (1969) 1.

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