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QUANTITATIVE PYROLYSIS GAS CHROMATOGRAPHY OF SOME TERE- POLYMERS AND THREE-COMPONENT POLYACRYLIC MIXTURES

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SUMMARY

The degradation behaviour of polyacrylic terepolymers and their homopolymer mixtures has been examined using a Curie Point pyrolysis system. A technique for distinguishing between copolymers and their homopolymer mixtures and then allowing calculation of polymer composition from pyrolysis data is shown to be applicable to three-component terepolymer systems and to multi-component homopolymer mixtures.

INTRODUCTION

While Strassburger *et al.*¹ showed in 1960 that the yield of acrylate monomer was substantially increased when pyrolysis of a copolymer containing a polymethacrylate as compared to a mixture of the polymers of the same composition was carried out the development of a relationship using the data as a means of identification was much slower. Gatrell and Mao² later showed an approximately constant fractional recovery of acrylate monomer of about 40% from copolymer and 19.0% from homopolymer systems using a filament of estimated temperature 400-600°.

McCormick³ in 1969 demonstrated the possibility of pyrolysis and gas chromatography as a means of distinguishing mixtures of homopolymers from copolymers and showed some quantitative measurements, the procedure used—sequential pyrolysis of a single sample on a filament at increasing temperature with plots of monomer recovery and temperature—producing characteristic curves indicative of copolymers or homopolymers.

A Curie Point procedure has been reported⁴ which resembles that of McCormick³ in that the behaviour at various temperatures is considered, but where the disadvantages associated with temperature control of filaments are eliminated and the calculation of monomer yields at any temperature is facilitated. The use of three ferromagnetic wires of known Curie Point produces characteristic curves of monomer yield and temperature that allow identification as copolymer or polymer mixtures.

From the monomer recoveries a simple relationship described as the Homopolymer (HFI) or Copolymer Fragmentation Index (CFI) allows calculation from pyrolysis data of the composition of the unknown mixture or copolymer.

Terepolymer and other multicomponent systems find substantial industrial use but pyrolysis studies have not been reported. The present work shows the application of the Curie Point procedure to a terepolymer system and to homopolymer mixtures of the same composition. The structure of the polymer may be shown and the composition determined by the use of HFI or CFI values.

EXPERIMENTAL

Gas chromatography

Gas chromatography was carried out on a modified F & M 810/29 Research Chromatograph with flame ionisation detection and an improved flow control system. Two 12 ft. \times $\frac{1}{8}$ in. O.D. aluminium columns packed with 10% OV-1 on 60-80 mesh Chromosorb W were programmed between 100 and 220° at 10°/min with the top temperature held for 5 min before automatic recycling occurred. Helium was used as carrier gas at 40 ml/min. The amplifier sensitivity used was 16×10^2 A f.s.d. for methacrylate polymers and 2×10^2 A f.s.d. for minor components of acrylate polymers.

Radiofrequency pyrolysis

A Philips Curie Point pyrolyser was used. The ferromagnetic sample probes were prepared by forming a flat surface with light hammering for lengths of 1 cm at the end of the wires and then folding back these prepared tips to form a closed loop.

Solutions of the polymers were prepared and 0.50 ± 0.02 μ l of solution was deposited on wires with Curie Points of 480°, 610° and 770°. The amount of polymethyl methacrylate deposited from solution was determined to be 10 ± 0.4 μ g and the approximate film thickness was calculated to be 0.5 μ . The coated wires were stored for 24 h to allow evaporation of solvent and the residual material was removed by allowing several minutes to elapse after mounting in the pyrolysis head prior to firing.

RESULTS

Terepolymers of three monomers, methyl methacrylate, 2-ethylhexyl acrylate, and ethyl acrylate were prepared containing relative molar ratios of 5:3:1, 3:3:3, and 1:3:5. Corresponding sets of homopolymer mixtures of the same compositions were prepared together with blends of a copolymer of methyl methacrylate and ethyl acrylate (1:1) with poly-2-ethylhexyl acrylate in the ratio 2:1 to form a product with relative mole ratios of components 1:1:1 and of a copolymer of methyl methacrylate and 2-ethylhexyl acrylate with polyethyl acrylate in the same proportions.

Pyrolysis of the samples was carried out at 480°, 610° and 770°. The monomer yields obtained at 610° are shown in Table I while the yields obtained at the three temperatures are shown in Fig. 1. From the plots of the copolymer yields it is apparent that the three monomers in each case show maximum recoveries near 610° while with the corresponding homopolymer mixtures the maxima are dependent on the chemical

TABLE I

MONOMER YIELDS FROM THREE-COMPONENT TEREPOLYMERS AND HOMOPOLYMER MIXTURES

Relative molar ratios			Percentage yield at 610°					
M_1 Methyl methacrylate	M_2 2-Ethylhexyl acrylate	M_3 Ethyl acrylate	Copolymers			Homopolymers		
			M_1	M_2	M_3	M_1	M_2	M_3
5	3	1	96	20	25	96	8	11
3	3	3	96	18	24	95	8	11
1	3	5	93	14	20	94	7	9
3	3	3	98	—	28	—	7	—
3	3	3	97	20	—	—	—	11

type of the monomer, *i.e.* the methyl methacrylate showed a maximum near 610° while the acrylate monomers exhibit separate and higher maxima near 777°. These behaviours are identical to those experienced with copolymers and their corresponding homopolymer mixtures⁴ and clearly show the composition of the sample as a terpolymer or mixture of polymers.

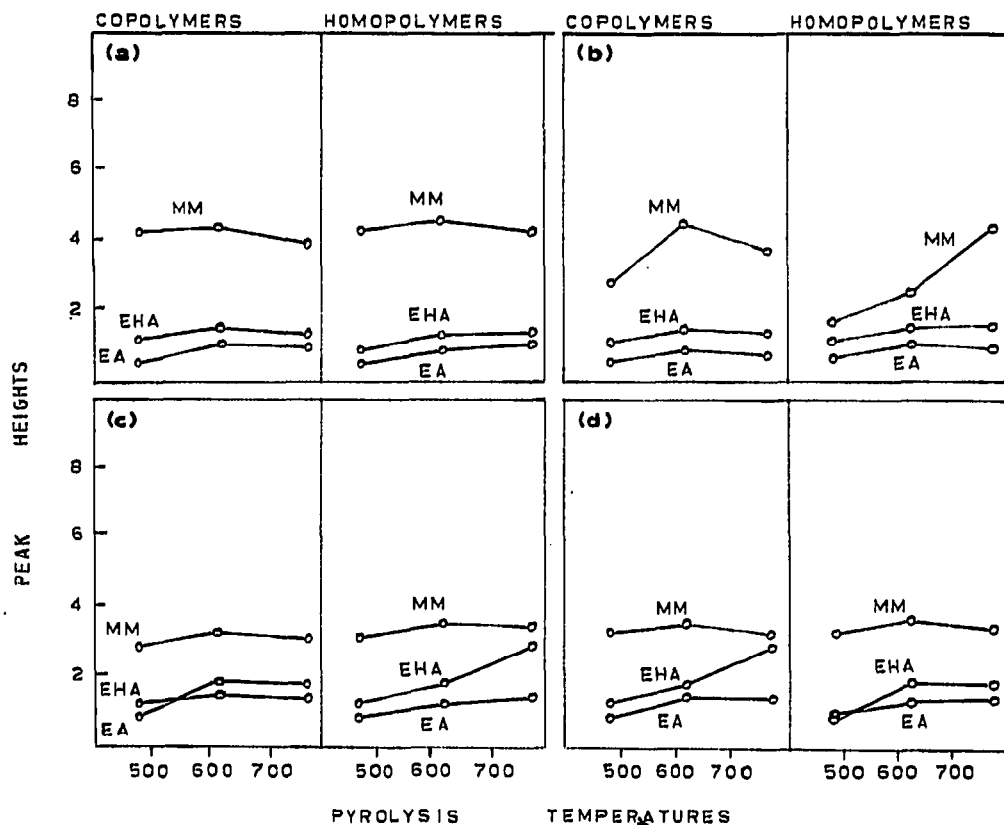


Fig. 1. Monomer yields from the pyrolysis of terpolymers and homopolymer mixtures at 480°, 610°, and 770°. MM = Methyl methacrylate, EHA = 2-ethylhexyl acrylate, and EA = ethyl acrylate.

Fig. 1d shows the pyrolysis yields of two polymer systems of equimolar composition, and as the polymers shown in Fig. 1b but each consisting of a copolymer and a homopolymer acrylate. The yield curves for these mixtures are different from those shown in Fig. 1b. The methyl methacrylate curves are as expected, the yields being independent of the polymer structure, the curves of the two acrylate comonomers differ, the ethyl acrylate known to be present as a copolymer, shows the expected increase in monomer yield with increased temperature while the homopolymer poly-2-ethylhexyl acrylate produces monomer with maxima near 610°. Conversely, where the 2-ethylhexyl acrylate is present in the copolymer, increased monomer yield with temperature is evident while the ethyl acrylate yields shows a maxima near 610°.

The difference in pyrolysis behaviour clearly shows the presence of a monomer in an unknown system as a constituent of a copolymer or terpolymer or simply as a homopolymer in admixture.

Following identification of the polymer structure the true polymer composition is calculated by the mathematical correction factors which have been described as The Homopolymer Fragmentation Index and The Copolymer Fragmentation Index⁴.

From previously calculated mass response factors of the flame ionisation detector the peaks obtained on the chromatogram from the pyrolysis at 610° of the terpolymer of methyl methacrylate, 2-ethylhexyl acrylate, and ethyl acrylate in the ratio 5:3:1 indicated that 5.4 μg (0.054 μmoles) of methyl methacrylate, 1.2 μg (0.0067 μmoles) of 2-ethylhexyl acrylate and 0.3 μg (0.003 μmoles) of ethyl acrylate were produced by the use of the Copolymer Fragmentation Index for each monomer (Table II):

Amount of methyl methacrylate present in polymer = $0.054 \times 1.02 = 0.055$ μmoles .

Amount of 2-ethylhexyl acrylate present in polymer = $0.0067 \times 5.0 = 0.0335$ μmoles .

TABLE II

HOMOPOLYMER (HFI) AND COPOLYMER (CFI) FRAGMENTATION INDICES OF MONOMERS

Mean values from concentrations 10% to 100%.

	HFI	CFI
Methyl acrylate	7.0	2.5
Ethyl acrylate	8.9	3.7
Propyl acrylate	9.4	3.9
Butyl acrylate	10.0	4.1
Pentyl acrylate	9.8	4.2
Hexyl acrylate	8.0	4.3
2-Ethylhexyl acrylate	14.0	5.0
Methyl methacrylate	1.02	1.02
Ethyl methacrylate	1.02	1.02
Propyl methacrylate	1.02	1.02
Butyl methacrylate	1.02	1.02
Pentyl methacrylate	1.03	1.03
Hexyl methacrylate	1.03	1.03
2-Ethylhexyl methacrylate	1.04	1.04

Amount of ethyl acrylate present in polymer = $0.003 \times 3.7 = 0.011 \mu\text{moles}$.
The original proportion of monomer molecules is thus shown to be 5:3:1.

The efficiency of recovery of the pyrolysis products may be calculated from the same example. The original amounts of monomer indicated in μg are: methyl methacrylate (0.055×100) 5.5, 2-ethylhexyl acrylate (0.0335×184) 6.3, and ethyl acrylate (0.011×100) 1.1, indicating essentially quantitative recovery.

If the sample had been erroneously identified as a mixture of homopolymers the methyl methacrylate would still have been estimated as 0.055 μmoles but the 2-ethylhexyl acrylate and ethyl acrylate would have been (0.0067×14.0) 0.094 and (0.003×8.9) 0.027 μmoles , respectively. The recovery in μg indicated would thus have been methyl methacrylate 5.5, 2-ethylhexyl acrylate 17.3, and ethyl acrylate 2.7, while the overall recovery of 25.5 μg is slightly in excess of twice the original sample weight.

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