Qualitative and Quantitative Analysis of Methyl Acrylate or Methyl Methacrylate of Acrylonitrile Fibers by Pyrolysis Gas Chromatography

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Synopsis

Degradation gases evolved from methyl acrylate or methyl methacrylate of acrylonitrile fibers were analyzed by pyrolysis gas chromatography. For determining polymer composition, optimum pyrolysis conditions were determined and calibration was accomplished by using acrylonitrile–methylacrylate and acrylonitrile–methyl methacrylate model copolymers. Out of the 23 samples examined, 10 were found to contain methyl acrylate and five methyl methacrylate comonomers, in the range of 3.5–8.0%. The reproducibility of the method was good, the coefficient of variations was ∓2% for methyl acrylate and ∓2.5% for methyl methacrylate. Compositions were in agreement with those determined by other methods.

INTRODUCTION

Polyacrylonitrile fibers are usually produced in the presence of comonomers such as methyl acrylate (MA), methyl methacrylate (MMA), and vinyl acetate (VAc) and the amount of these comonomers can be as high as 15%. To make a successful curing and dyeing process, it is important to know the type and amount of these comonomers. Since the chemical degradation of polyacrylonitrile chains is difficult and the comonomer contents are variable, the analysis of these comonomers is more difficult as compared to polyester and polyamide fibers.

In the early works, the analyses of the comonomers were performed either indirectly by determining the nitrogen content of the fibers or directly by examining the ester groups using IR spectra. However, the first method is long and tedious and, hence, subject to errors.[1,2] In the IR method,[3-5] carbonyl contents are usually over estimated due to the presence of carbonyl containing binding agents, used for dyeing.

Later studies developed chemical methods for the determination of VAc, MA, and MMA. The determination of VAc was accomplished by heating the fibers in a closed vessel at 160°C for 3 h in the presence of *p*-toluenne-sulphonic acid and then determining the acetic acid produced by gas chromatography.[6] Analysis of MA and MMA was carried out by measuring methanol, produced by heating the fiber with 100% hydrazine hydrate in a closed system at 100°C for 7 h, and the results were used for the calculation of the comonomer contents.[7]

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Pyrolysis gas chromatography is one of the methods that has been used for a long time to investigate the qualitative and quantitative analysis of polymers. The thermal degradation of the copolymers of MA, MMA, and VAc with AN and its mechanism have already been investigated. However, the MA, MMA, or VAc contents of the examined copolymers are very different from those of polyacrylonitrile fibers. So far, however, for AN–MMA copolymer only one pyrolysis gas chromatographic analysis result with over 80% AN content was reported.[8] In the above-mentioned work MMA content has been reported to be found with an error of 7.2%. Previously we reported the pyrolysis gas chromatographic determination of VAc content of polyacrylonitrile fibers with an error of ∓2.5%.[9] In this work, we report a similar study of the polyacrylonitrile fibers containing MA and MMA comonomers.

EXPERIMENTAL

Studies were carried out on a "Pyromatik" (Fischer made) pyrolysis apparatus, combined with a Perkin-Elmer F-7 gas chromatograph. Model copolymers of AN–MA and AN–MMA, necessary for the investigation of the polyacrylonitrile fibers, were prepared from the monomers, using peroxydisulfate, metabisulfite, and Fe^{2+} catalyst systems, analogous to the industrial process.[10] The copolymers and fibers were purified by extraction first with methanol then with acetone for 6 h and then were dried at 60°C and 30 mm Hg for 12 h.

MA or MMA contents of these copolymers were found by the gas chromatographic analysis of methanol, formed by the hydrolysis of the ester groups.[7] The results are shown in Table I.

In the experiments, 5–20 μL solutions of 0.1 g polystyren as an internal standard and 1 g fiber or copolymer in 100 mL N,N-dimethylformamide

TABLE I
Constituents of Model Copolymer

	Percentage of constituents		
Model copolymer	AN	MA	MMA
1	99.50	0.50	
2	97.00	3.00	
3	94.00	6.00	
4	91.00	9.00	
5	87.60	12.40	
6	85.00	15.00	
7	82.70	17.30	
8	79.80	20.20	
9	98.75		1.25
10	97.03		2.97
11	92.75		7.25
12	92.10		7.90
13	89.60		10.40
14	87.10		12.90
15	84.80		15.20
16	83.34		16.66
17	82.25		17.75

(DMF) were dropped on the platinum spiral of pyrolysis injector to minimize the weighing errors and simplify the sample filling. Then, spiral was heated to 100–120°C three or four times for the periods of 20 s to remove the solvent completely. The dried sample pyrolyzed and products were carried to column by the carrier gas. Evaluations were based on the ratio of the peak areas of MA or MMA to peak area of styren.

In the experimental study, 15% D-*n*-decilphthalate, porapac Q, 10% carbowax, PEG 1500 columns were tested for the best selective separation of MA from styren and unknown other products and PEG 1500 was found to be the best. Among the porapac Q, 15% Apiezon L, 4% OV-1 columns, 4% OV-1 was the best selective column for MMA and styren monomers.

In order to find the optimum working conditions with a minimum total error, the pyrolysis temperature, time, and quantity of sample were all tested as parameters, and the most suitable temperature was noted as 600°C from 400 to 700°C with intervals of 50°C.

It was observed the pyrolysis time has no effect on the MA or MMA monomer yields by the tests tried from 10 to 20 s with the intervals of 2 s.

Since the monomer MA or MMA linearly increased by increasing the quantity of pyrolyzed sample from 0.025 up to 0.4 mg, a 0.05 mg sample for MMA copolymers and 0.2 mg for MA copolymers were found to be the most suitable sample sizes.

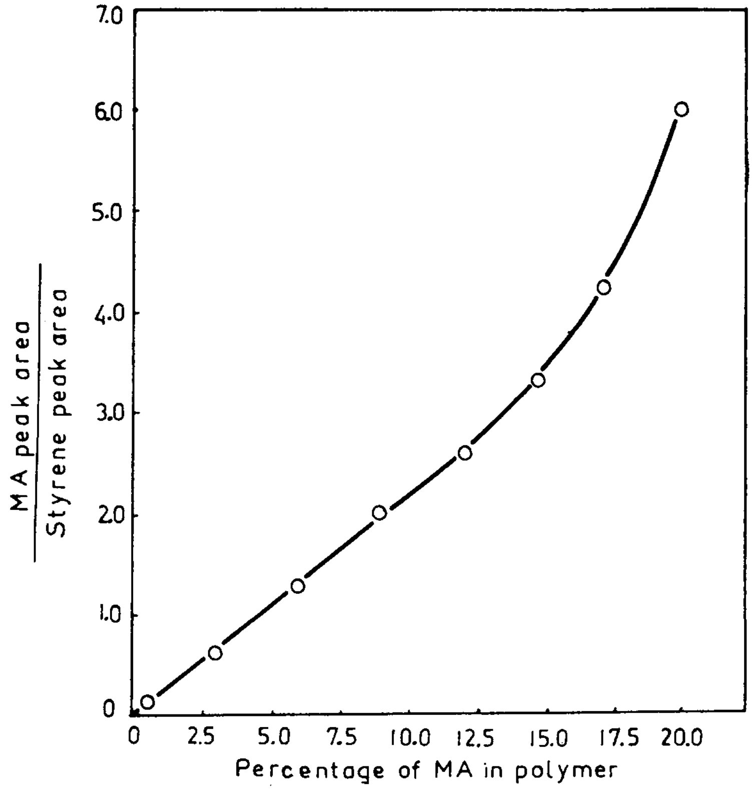

Fig. 1. Variation of MA formation with copolymer composition.

Working conditions for pyrolysis gas chromatography determined by the experiments for each copolymer type are shown below.

For MA Comonomer. Column, 1 m, PEG 1500. Column temperature: start isothermal at 60°C, after the 18th minute, heated to 100°C at a rate of 22.5°C/min. Detector and temperature, FID, 250°C; carrier gas, nitrogen at 25 mL/min; detector sensitivity, 1/4 for MA, 1/256 for styrene; pyrolysis temperature, 600 ∓ 5°C. Pyrolysis time, 20 s; sample size: 0.2 mg.

For MMA Comonomer. Column, 2 m, OV-1, 4%; column temperature, 50°C; detector and temperature, FID, 250°C; carrier gas, nitrogen at 25 mL/min; detector sensitivity, 1/4 for MMA, 1/32 for styrene; pyrolysis temperature, 600 ∓ 5°C; pyrolysis time, 20 s; sample size, 0.05 mg.

RESULTS AND DISCUSSION

The standard plots, prepared with model copolymers were used for determination of MA and MMA contents of the fibers. Figures 1 and 2 show the standard plots for AN-MA and AN-MMA copolymers respectively. It can be seen from Figure 1 that the MA contents of the pyrolysis products were increased linearly for the copolymers containing up to maximum of 13% MA and up to 11% for MMA. For the copolymers containing higher MA and MMA comonomers, a rapid formation of MA and MMA were observed during the pyrolysis.

The higher rate of monomer formation as seen from the parts of both curves is due to the change in the tacticity of MA or MMA monomers in chain. Each monomer molecule was surrounded by AN monomers in the low MA or MMA concentrations while in higher concentrations of MA or MMA, blocking

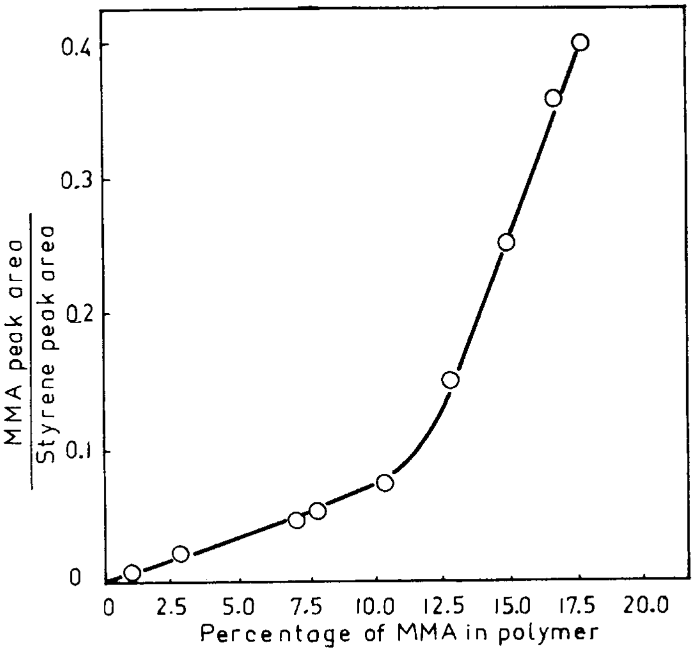

Fig. 2. Variation of MMA formation with copolymer composition.

character should be more possible. The copolymers having the low MA or MMA comonomers should have more homogeneous distribution in chain and therefore on platinum wire surface, to give a specific yield of monomer. The copolymers which have higher MA and MMA contents as blocks in chains, should give a nonhomogeneous film cast and domain structure depending to the solvent from which the film is cast.

As a result of nonhomogenity and the blocking character of comonomers in chain, the monomer yield of pyrolyzed copolymers should be nearly similar to the monomer yield of pyrolysis of homopolymers. However, the same effect can be seen in the pyrolysis of noncompatible homopolymer mixtures which are cast from the same solvent.

Considering that the polyacrylonitrile fibers contain no less than 85% AN according to DIN 60001 and ISO 2076-1973, the sum of additives and the comonomers should not exceed 15%. Therefore, MA and MMA contents of the fibers could be determined accurately from the first parts of the curves of Figures 1 and 2. Figures 3 and 4 show pyrograms of three different AN–MA and AN–MMA copolymer compositions.

In this work, several fibers, produced in different countries by 12 companies were investigated, and it was shown that fibers designated as, Aksa, Acrylan

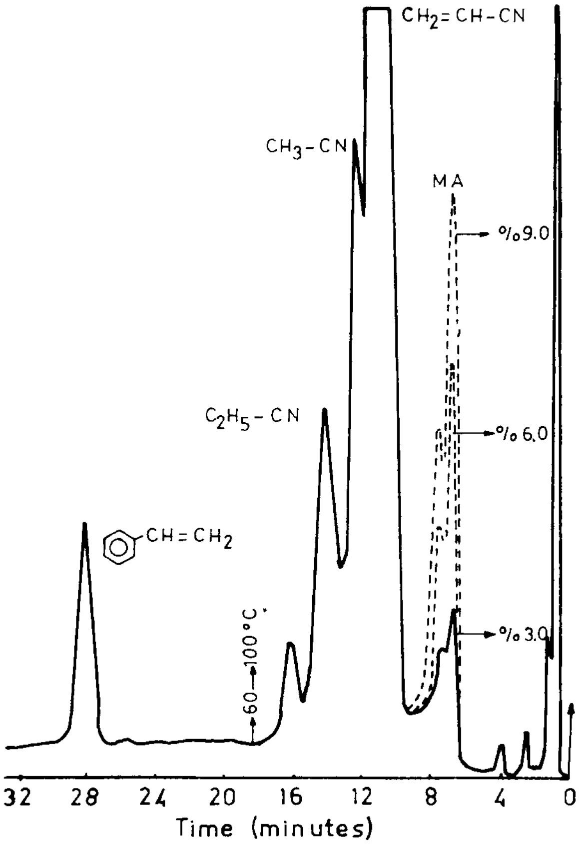

Fig. 3. Pyrogram of AN–MA copolymers.

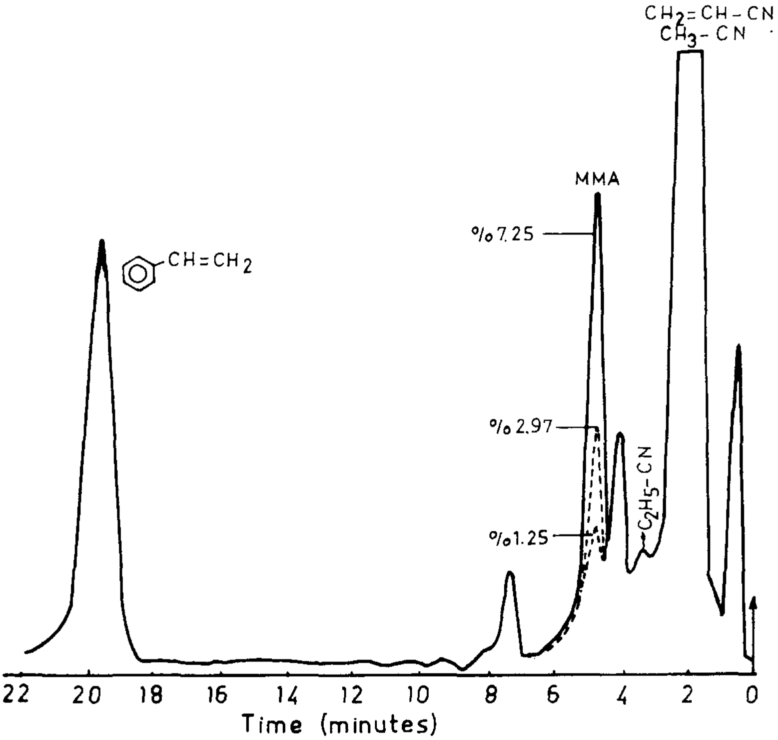

Fig. 4. Pyrogram of AN–MMA copolymers.

TABLE II
MA and MMA Contents of Polyacrylnitrile Fibers

Fiber name	Comonomer type	Percentage of comonomer: Pyrolysis gas chromatography	Chemical method	IR method
Orlon T 28	MA	4.8	5.1	4.8
Euracryl FG	MA	7.5	7.5	7.6
Euracryl RG	MA	7.0	6.9	6.9
Yalova Elyaf	MA	7.9	8.0	7.9
Orlon 75	MA	5.6	5.8	5.7
Dolan 20	MA	5.8	5.7	5.7
Courtella	MA	5.5	5.5	5.5
Dralon N	MA	4.9	5.1	5.0
Dralon DD	MA	4.9	4.8	4.9
Dralon BF	MA	3.6	5.1	5.0
Acrybel RG 150	MMA	4.0	4.4	3.9
Acrybel AT 708	MMA	4.1	4.3	—
Acrybel AT 928	MMA	3.9	4.0	—
Creslan	MMA	8.1	8.2	8.1
Crylor T 410	MMA	5.1	5.4	5.1

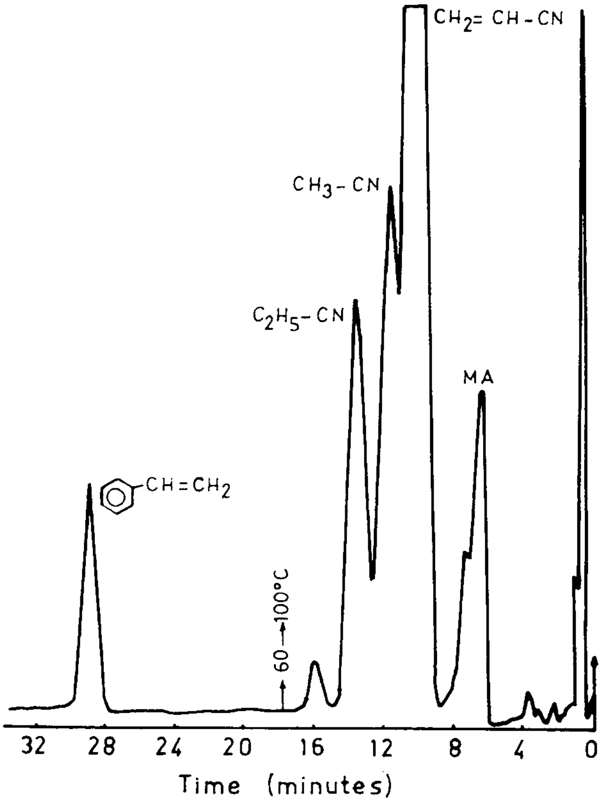

Fig. 5. Pyrogram of Dralon N.

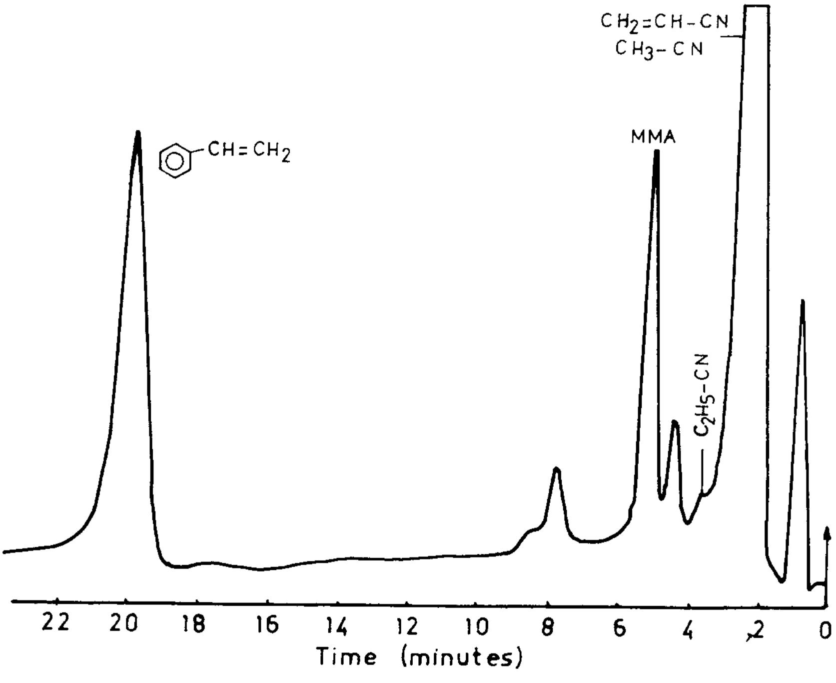

Fig. 6. Pyrogram of Creslan.

B-16, Acrylan B-57, Acrylan B-71, Euracryl FDT, and Leacryl did not contain any MA and MMA comonomers. Others which contain these comonomers are given in Table II.

Chemical and spectroscopic findings from the literature are also shown,[4,7] and it is seen that there is a good agreement except for the value for Dralon BF. The reason for this difference is due to the excess methanol hydrolyzed from the metoxy groups containing acidic additives which are added to improve the dyeability of Dralon BF.[11,12] As is seen, the pyrolysis gas chromatography method provides more reliable results by measuring directly the content of comonomers.

In order to show the reliability of the method Dralon N and Creslan fibers were analyzed 20 times each and the results were 4.9 ∓ 0.1 for MA comonomer and 8.1 ∓ 0.2 for MMA comonomer. Figures 5 and 6 show the pyrograms of these two fibers.

The results show that pyrolysis gas chromatography is a very suitable method for the determination of the comonomer contents of fibers since it takes relatively short time.

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