

PYROLYSIS--GAS CHROMATOGRAPHY OF VINYL
CHLORIDE-METHYL METHACRYLATE AND VINYL
CHLORIDE-ACRYLONITRILE COPOLYMERS

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Progress in polymerization techniques has gradually made it possible to control the sequential structures of polymers. A typical example is the complexed copolymerization¹ of vinyl compounds with alkylaluminum halides or related metal halides. This complexed copolymerization gives equimolar copolymers with an alternating sequential structure. Some of these alternating copolymers have excellent properties^{2,3}, because of the regularity in their structural units. In the future, the sequential structure of polymers may be more easily controlled, and it must become increasingly important to analyze the microstructure. Pyrolysis--gas chromatography is one of the most powerful methods for the analysis of the microstructure of polymers.

The pyrolysis--gas chromatographic behaviours of *cis*-1,4-, *trans*-1,4- and 1,2-polybutadienes⁴ and of random and alternating copolymers of acrylonitrile and butadiene have already been reported⁵. In this paper, the relationships between pyrolytic products and microstructures have been investigated by means of pyrolysis--gas chromatography for copolymers of vinyl chloride with methyl methacrylate or acrylonitrile.

EXPERIMENTAL

Materials

Random copolymers of vinyl chloride (VC)-methyl methacrylate (MMA) and of VC-acrylonitrile (AN) were synthesized by bulk polymerization with azobis(isobutyronitrile) as initiator. Alternating VC-MMA copolymer⁶ was prepared in the presence of ethylaluminum dichloride-vanadium oxytrichloride, and alternating VC-AN copolymer⁷ in the presence of ethylaluminum dichloride by established methods.

Table I shows the copolymer compositions calculated from the elemental analyses.

Apparatus and technique

A curie-point pyrolyzer (Nippon Bunseki Kogyo JHP-2) was used to decompose the polymers. This gives reproducible pyrograms because the fast temperature rise (curie-point of the ferromagnetic wire) results in more specific products

TABLE I

ANALYTICAL DATA FOR VC-MMA AND VC-AN COPOLYMERS

Sample ^a	C (%)		H (%)		N (%)		VC (mole-%)
	Found	Calcd.	Found	Calcd.	Found	Calcd.	
<i>VC-AN Copolymer</i>							
R ₁	60.9	61.0	5.5	5.5	20.2	20.2	20.8
R ₂	55.7	55.7	5.3	5.3	15.5	15.5	37.5
R ₃	51.7	52.0	5.2	5.2	12.1	12.1	50.7
R ₄	49.1	49.0	5.1	5.2	9.4	9.5	60.3
R ₅	42.1	42.1	5.0	5.0	3.3	3.3	85.6
A	52.0	52.0	5.1	5.2	12.3	12.2	49.9
<i>VC-MMA Copolymer</i>							
R ₁	56.4	56.7	7.8	7.6			22.5
R ₂	52.4	52.6	7.1	7.0			45.7
R ₃	50.6	50.7	6.7	6.7			55.0
R ₄	48.1	48.3	6.5	6.3			65.6
A	51.9	51.8	6.8	6.9			49.4

^a R = Random copolymer, A = alternating copolymer.

and any contamination from previous samples can be avoided by using a new wire each time. The pyrolyzer was coupled to a gas chromatograph (Shimadzu GC-4BM) equipped with a dual flame-ionization detector. The samples were 10-20 μ g in size.

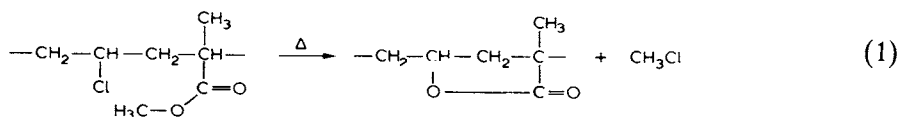
The separation column was stainless steel tubing (75 cm x 3 mm i.d.), packed with Porapak N (100--120 mesh). A column (5 cm x 3 mm i.d.) packed with a mixture of K₂CO₃ and Diasolid H(60--80 mesh) in a 1:2 weight ratio was placed between the pyrolyzer and the separation column to precut acidic products on pyrolysis. The separation column was operated at 170 °C and the detector block was maintained at 220 °C. The flow rate of carrier gas (nitrogen) was 30 ml min⁻¹ and the hydrogen and air pressures were 0.5 kg cm⁻² and 1.0 kg cm⁻² respectively. The peak areas were measured by a digital integrator (Shimadzu ITG-4A).

Identification of the peaks was carried out by comparison with the retention data of known substances and/or by direct combination of the pyrolysis-gas chromatograph with a mass spectrometer (Nippon Bunko-Finnigan GC-9500-3100D)

RESULTS AND DISCUSSION

VC-MMA copolymer

Zutty and Welch⁸ reported that when VC-MMA copolymers are heated at 150-200 °C, an intramolecular lactonization from adjacent co-monomers occurs, forming γ -butyrolactone groups in the polymer backbone concomitant with the quantitative elimination of methyl chloride (eqn. 1).



The extent of this cyclization depends on the arrangement of the monomer units in the copolymers. The copolymers listed in Table I were heated under vacuum at 200 until lactonization was complete, and no further weight loss was observed. From this weight loss, the fraction of the methyl methacrylate units cyclized, $f_c(\text{MMA})$, was calculated. These experimental $f_c(\text{MMA})$ values were in good agreement with the theoretical ones given from a statistical treatment^{9,10} based on the expected number of adjacent MMA and VC residues, as shown in Table II.

Figure 1 shows typical pyrograms of random (R2) and alternating VC-MMA copolymers (pyrolysis at 541 °C). The yields of MMA monomer, methyl chloride

TABLE II

LACTONIZATION OF VC-MMA COPOLYMERS

Sample	Composition MMA (mole-%)	$f_c(\text{MMA})^a$	
		Experimental	Theoretical ^b
R ₁	77.51	0.235	0.276
R ₂	54.34	0.567	0.629
R ₃	45.03	0.731	0.757
R ₄	34.44	0.873	0.870
A	50.60	0.860	0.865

^a $f_c(\text{MMA})$ represents the fraction of the methyl methacrylate units cyclized.

^b See Refs. 9 and 10 for details.

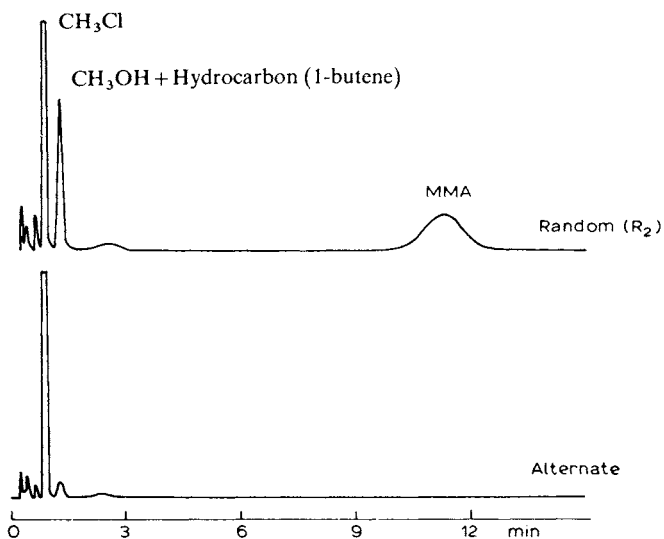


Fig. 1. Pyrograms of VC-MMA copolymer at 541°C.

PYROLYSIS PRODUCTS OF VC-MMA COPOLYMERS AT 541°C

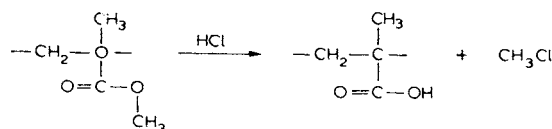
Sample	Yield of pyrolysis products (mole-%) ^a		
	MMA	CH ₃ Cl	CH ₃ OH ^b
R ₁	26.1	24.7	9.2
R ₂	7.5	66.9	14.0
R ₃	3.9	72.1	11.1
R ₄	0.5	60.5	3.9
A	0.6	71.5	0.5

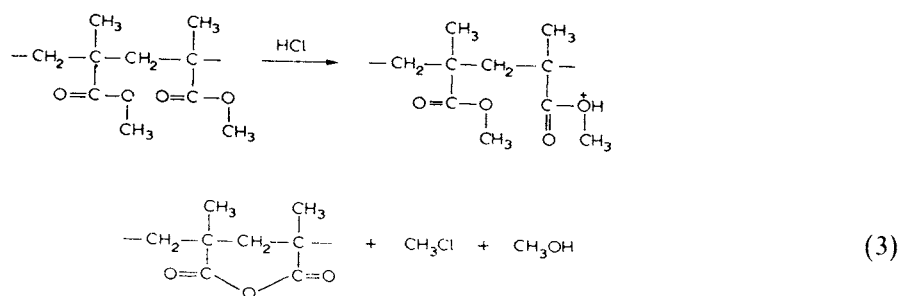
^a Mole-% to MMA in copolymer.

^b Obtained indirectly from the decrease in peak area after methanol had been removed with an absorber (15 cm × 3 mm i.d.) packed with 25% PEG-20M on Celite 545 (60-80 mesh) containing 3 wt.% boric acid, placed before the separation column.

and methanol on the pyrogram are summarized in Table m, and expressed in terms of mole percentage to MMA in the copolymer. In the case of the random copolymers, it is reasonable that the MMA yield decreases with the decrease of MMA content in the sample. The yields of methyl chloride and methanol reach maxima near 50 mole-% of MMA content. But the alternating copolymer gives only negligible amounts of MMA and methanol, though it yields methyl chloride in amounts between those of R₂ and R₃.

These results may be interpreted as follows. The alternating copolymer contains only a VC-MMA unit in its chain, and has a larger $f_c(\text{MMA})$ value than the random copolymers with compositions close to the alternating one, as shown in Table II. It is therefore assumed that the production of MMA monomer from the alternating copolymer is reduced because of both the absence of the unzipping reaction from the successive MMA unit and the lesser extent of the uncyclized MMA units. There is no difference in the methyl chloride yields of the random and alternating copolymers, hence methyl chloride must be produced by other mechanisms predominantly occurring in the random copolymer in addition to the lactonization reaction. Reactions (2) and (3) were proposed by McNeil and Neil¹¹ from the results of the pyrolysis for PVC-PMMA blends, but they could not confirm the production of methanol. In the present tests of pyrolysis at 541°C, the 1:1 PVC-MMA blend gave methyl chloride, methanol and MMA in molar ratios of 0.393, 0.166 and 1.000, respectively; but methyl chloride and methanol were obtained from neither PVC nor PMMA. As shown in eqns. (3), methanol is given by the attack of hydrogen chloride from dehydrochlorination of VC units on the MMA-MMA unit together with equal amounts of methyl chloride. If the methanol yield (Table) is considered, the contribution of eqn. (3) to the formation of methyl chloride cannot be neglected in the case of the random copolymers. It was found, as mentioned above, that the microstructural differences are reflected on the pyrograms.





VC-AN copolymer

The thermal degradation of polyacrylonitrile and acrylonitrile containing copolymers has been studied extensively¹²⁻¹⁴, and many kinds of degradation products including dimers have been found. In the present work, the random and alternating VC-AN copolymers listed in Table I were pyrolyzed at 536 °C, but did not give dimers as degradation products (Fig. 2). The main products of the random copolymers are AN monomer and acetonitrile. Figure 3 shows the relationship between the molar ratio of acetonitrile to AN monomer on the pyrogram and the VC content of the copolymer. This ratio increases suddenly as the VC content exceeds 50 mole-%. It is suggested that AN monomer is produced from AN--AN units at least. In fact, the alternating copolymer having only a VC--AN unit gives no peak of AN monomer on the pyrogram, but only acetonitrile.

It is interesting to note that methyl chloride is obtained from the alternating samples as a main product but hardly at all from the random samples. The alternating copolymer gives a resinous solid on heating at 320 °C for 3 min under

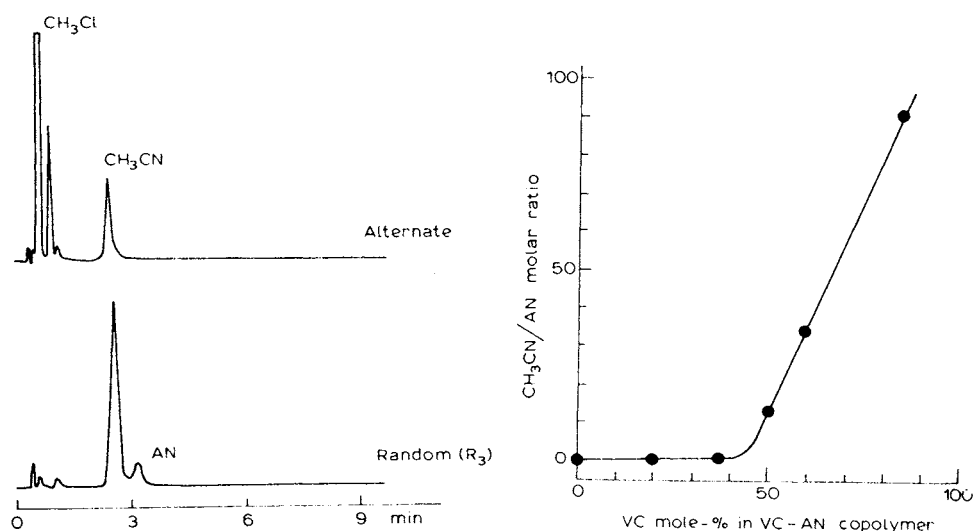


Fig. 2. Pyrograms of VC-AN copolymer at 536°C.

Fig. 3. CH₃CN/AN molar ratio of VC-AN copolymers (random) on pyrograms at 536°C.

a nitrogen atmosphere. When this resinous solid is pyrolyzed at 536 °C, the main product is acetonitrile and only a little methyl chloride is formed. It is assumed from this result that methyl chloride is eliminated first, and that the residual substance has a structure from which acetonitrile is produced easily on pyrolysis.

Further work is being done to elucidate the specific degradation mechanism of the alternating VC-AN copolymer.

SUMMARY

Pyrolysis-gas chromatographic investigations have been carried out on VC-MMA and VCAN copolymers with a curie-point pyrolyzer. The pyrograms distinctly show the difference in sequential structures of these copolymers. MMA monomer and methanol are scarcely formed from the alternating VC-MMA copolymer; the alternating VC-AN polymer yields mainly methyl chloride, which is not obtained from the random samples. The microstructure of copolymers in relation to their degradation products is discussed.

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