

Analysis of Sequence Distribution in Acrylonitrile-Fluoroacrylate Copolymer by Pyrolysis Gas Chromatography

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The sequence distribution of acrylonitrile-methylacrylate (AN-EA) copolymer and acrylonitrile-fluoroacrylate (AN-FA) copolymer were investigated by means of Curie-point pyrolysis gas chromatography (PGC). On the basis of the obtained pyrograms, run numbers and average chain length of copolymers were estimated from the relative intensities among the monomer peaks and the dimer peaks, respectively. It was found that AN-FA copolymer has much larger average run numbers than that of AN-EA copolymer (60 and 40, respectively). These data suggest that AN-FA copolymer should have comparably high alternative structures.

1 Introduction

The studies of the sequence distribution of copolymers have been frequently performed by ^{13}C -NMR spectroscopy. By this method, the change of chemical shifts of the skeletal carbons, between homopolymer and copolymer, is observed. But, it can not be applied to every kind of copolymers because of insolubility to organic solvents or of difficulty obtaining high resolution.

On the other hand, pyrolysis gas chromatography (PGC), which doesn't need organic solvents, has been recognized as a useful tool for the study of many copolymers. For example, in the case of acrylonitrile-methylacrylate (AN-MA) copolymers, Tsuge et al.(1) confirmed that the results obtained by PGC are compatible with the theory of copolymerization.

In this paper, in the first step, the average sequence length and run numbers

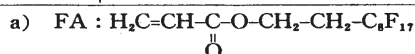
of acrylonitrile-ethylacrylate (AN-EA) copolymers were studied by relative intensities among the EA-EA, EA-AN, AN-AN dimer peaks. Here, the run number defined by Harwood(2) is the average number of monomer sequences (runs) occurring in copolymer per 100 monomer units. In the next step, this method was applied to acrylonitrile-fluoroacrylate (AN-FA) copolymers. The main peaks of pyrograms were assigned by PGC-MS.

2 Experimental

Samples. The three kinds of acrylonitrile-ethylacrylate (AN-EA) copolymers and of acrylonitril-fluoroacrylate (AN-FA) copolymers, and their homopolymers [polyacrylonitril (PAN), polyethylacrylate (PEA), polyfluoroacrylate (PFA)] were used as shown in Table 1. AN-EA and AN-FA copolymers and their homopolymers were prepared by free radical bulk polymerization at 60°C.

Table 1 Composition of the Copolymer Samples.

Sample No.	Sample	Mole Fraction in Feed		
		AN	EA	FA ^{a)}
1	PAN (Polyacrylonitrile)	1	—	—
2	PEA (Polyethylacrylate)	—	1	—
3	PFA (Polyfluoroacrylate)	—	—	1
4	AN-EA (1 : 2)	0.333	0.667	—
5	AN-EA (1 : 1)	0.500	0.500	—
6	AN-EA (2.4 : 1)	0.706	0.294	—
7	AN-FA (1 : 2)	0.333	—	0.667
8	AN-FA (1 : 1)	0.500	—	0.500
9	AN-FA (2.4 : 1)	0.706	—	0.294



Assuming pure radical copolymerization, the monomer reactivity ratios for AN-FA copolymer systems were experimentally determined ($r_{\text{AN}}=0.2$ and $r_{\text{AF}^*}=0.7$ for acrylonitrile and fluoroacrylate, respectively).

Apparatus. A Curie-point pyrolyzer (Japan Analytical Industry, JHP-2) was directly connected to a gas chromatograph (Hitachi, 663-30) with stainless packed columns and FID.

The peak assignment of the pyrograms were carried out by direct combination of the gas chromatograph with a mass spectrometer (Hitachi, RMU-6MG). The peak area of the resulting pyrograms were calculated by an integrator (Shimadzu, Chromatopack C-R 2 A).

PGC measurements conditions. The operating conditions are as follows :

(1) Detection of dimers for AN-EA and AN-FA copolymers

separating column : 1 m stainless tubing (3mm i.d.) packed with 20%
FFAP (free fatty acid polymer) on 60/80 mesh Di-
asolid M
column temperature : Programmed for 50° (4 min hold)-200°C at a rate
of 15°C/min
pyrolysis condition : pyrolysis temp., 650°C for 6 second
sample amount; 2mg
interface temp.; 190°C
carrier gas; N₂ (20 ml/min)

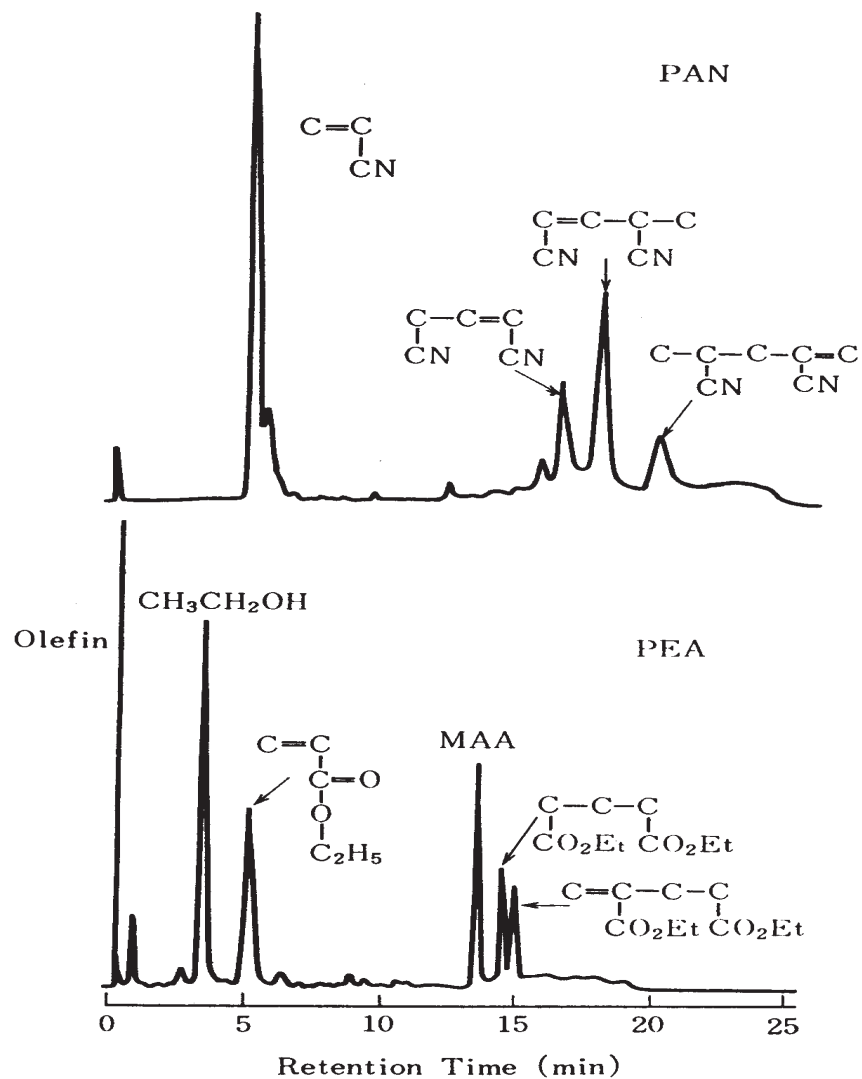
(2) Detection of AN monomer for AN-FA copolymer

separating column : 1.5m stainless tubing (3mm i.d.) packed with Pora-
pak QS
column temperature : programmed for 150-230°C at a rate of 10°C/min
pyrolysis condition : pyrolysis temp., 590°C for 5 second
sample amount; 2 mg
interface temp.; 150°C
carrier gas; N₂ (20 ml/min)

3 Results and Discussion

3.1 AN-EA copolymers

Figure 1 illustrates the pyrograms of polyacrylonitrile (PAN) and polyethylacrylate (PEA). The relative yields of monomers and dimers from these copolymers are summarized in **Table 2**. As shown in **Table 2**, the dimer yields of PAN and PEA are nearly equal. According to Tsuge et al.⁽³⁾, provided that the dyad (A-A, A-B, B-B) contents derived from A-B copolymer are equal, the relative yields of monomers and dimers by the pyrolysis of A and B homopolymer are almost equal. Therefore the theory of Harwood⁽²⁾ is applicable to AN-EA



Column Temperature : 50°C (4min hold) – 200°C (15°C/min)

Fig. 1 Typical pyrograms of PAN and PEA at 650°C.

Table 2 Relative Yields of Monomer and Dimer from PAN and PEA at 650°C.

Sample	Relative Yields	
	Monomer	Dimer
PAN	0.576	0.424
PEA	0.490	0.510

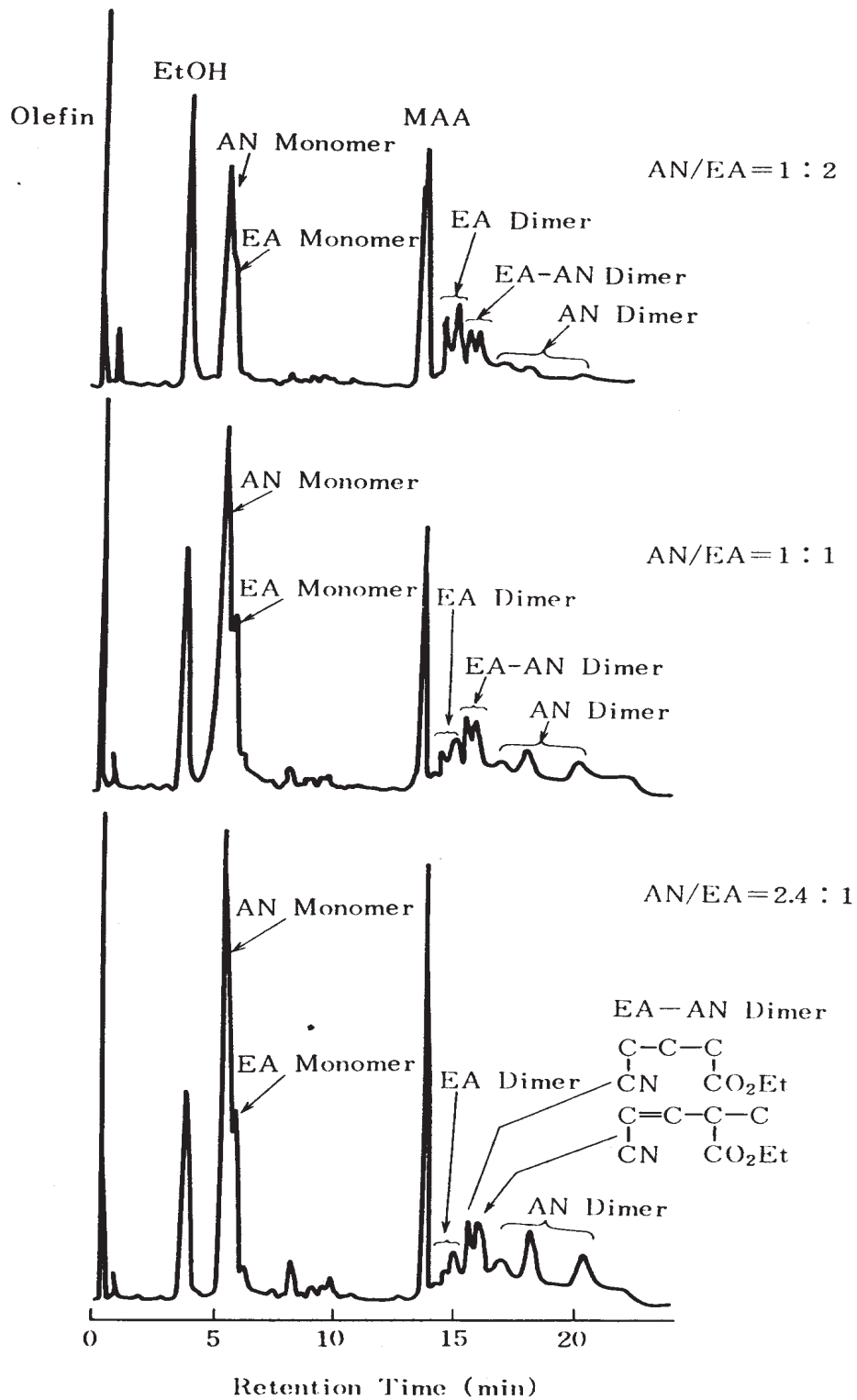


Fig. 2 Pyrograms of AN-EA copolymers at 650°C.

copolymers. According to their theory, the relative dimer yields are compatible with theoretical dyad concentrations, for some copolymer systems, in which the corresponding homopolymers have similar degradation characteristics. **Figure 2** shows the pyrograms of AN-EA (2 : 1) copolymer, AN-EA (1 : 1) copolymer and AN-EA (1 : 2.4) copolymer, at the pyrolysis temperature of 650°C. As for PEA and AN-EA copolymers, ethanol, methacrylic acid (MAA) and olefin etc. were produced by the pyrolysis. In this case, much attention is being denoted to the peaks of EA monomer and dimers. The structures of dimers derived from AN-EA copolymers were determined by PGC-MS and shown in **Fig. 3**.

Table 3 shows the relative yields of dimers from three AN-EA copolymers. From these data, run number and average sequence length of AN-EA copolymers were calculated and summarized in **Table 4**. These results suggest that the AN-EA (1 : 1) and AN-EA (2 : 1) copolymers have larger amounts of random chains than the AN-EA (1 : 2.4) copolymer.

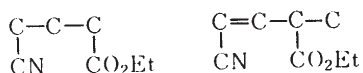


Fig. 3 Structures of AN-EA dimers.

Table 3 Relative Yields of Dimers from AN-EA Copolymers at 650°C.

Molar Ratios in Feed AN : EA	Relative Yields (%)		
	AN-AN	AN-EA	EA-EA
1 : 2	30	35	35
1 : 1	32	46	22
2.4 : 1	37	42	21

Table 4 Calculated Sequence Distribution Data of AN-EA Copolymers.

Molar Ratios in Feed (AN : EA)	$R^a)$	$\langle \text{AN} \rangle^b)$	$\langle \text{EA} \rangle$	$P_{\text{AN-AN}}^c)$	$P_{\text{AN-EA}}$	$P_{\text{EA-AN}}$	$P_{\text{EA-EA}}$
1 : 2	35	1.9	3.8	0.47	0.53	0.26	0.74
1 : 1	46	2.2	2.2	0.54	0.46	0.46	0.54
2.4 : 1	42	3.2	1.6	0.69	0.31	0.63	0.37

a) R : Run number

b) $\langle A \rangle$: Average chain length of A monomer

c) $P_{\text{A-B}}$: The ratio of A component which participate in A-B union

3.2 AN-FA copolymers

Figure 4 shows the pyrograms of PAN and polyfluoroacrylate (PFA). FA

monomer and FA-FA dimers from PFA could hardly be detected and many fluoro olefins and fluoro alcohols were produced by pyrolysis at 650°C, because the side chain was more easily scissored than the skeletal chain. Therefore, much attention is being denoted to the peaks of the AN monomer.

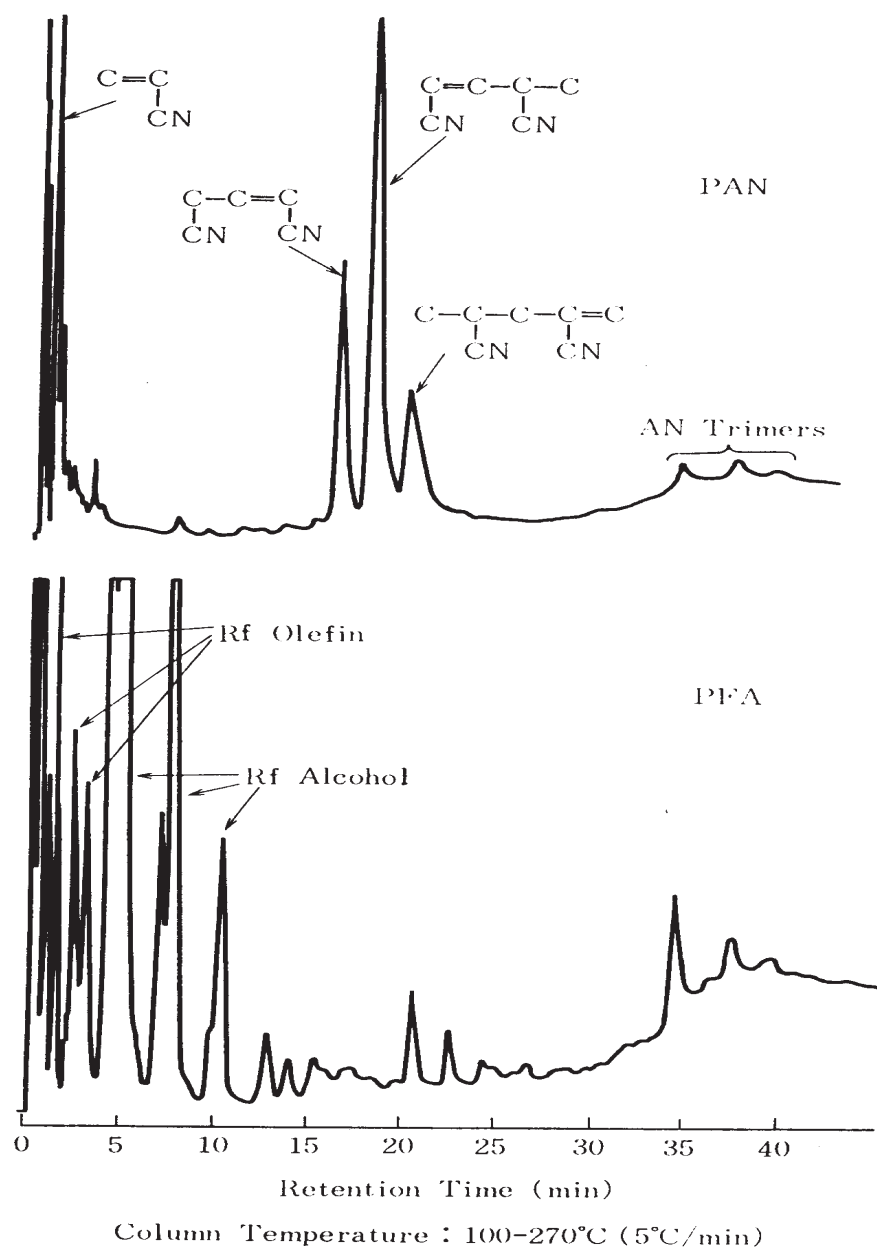


Fig. 4 Typical pyrograms of PAN and PFA at 650°C.

It has been generally recognized that at the most of copolymers, the yields of monomers reflect the copolymer composition. **Figure 5** shows the pyrograms of AN-FA (1 : 2) copolymer, AN-FA (1 : 1) copolymer and AN-FA (2.4 : 1) copolymer, under the condition of the pyrolysis temperature at 590°C. The starting amounts of monomer molar fractions (F_A) of feeded acrylonitril monomer

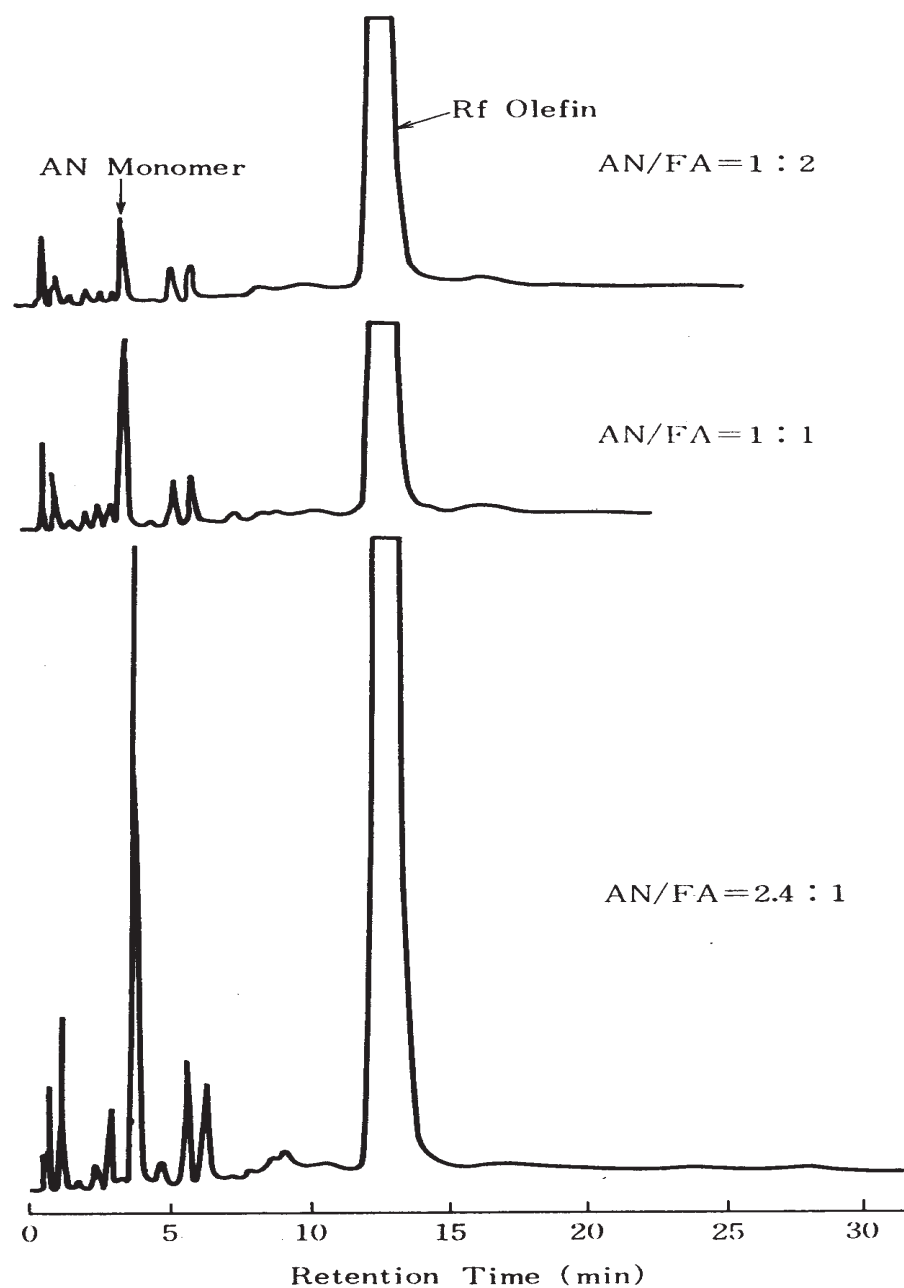


Fig. 5 Pyrograms of AN-FA copolymers at 590°C.

**Table 5 Area Intensities of AN Monomer
from AN-FA Copolymers at 590°C.**

Molar Ratio in Feed AN : FA	Molar Fraction (F_A)	Area Intensity ^{a)} ($C(A)$)
1 : 2	0.333	214
1 : 1	0.500	239
2.4 : 1	0.706	386

a) Count of peak area intensity by integrator

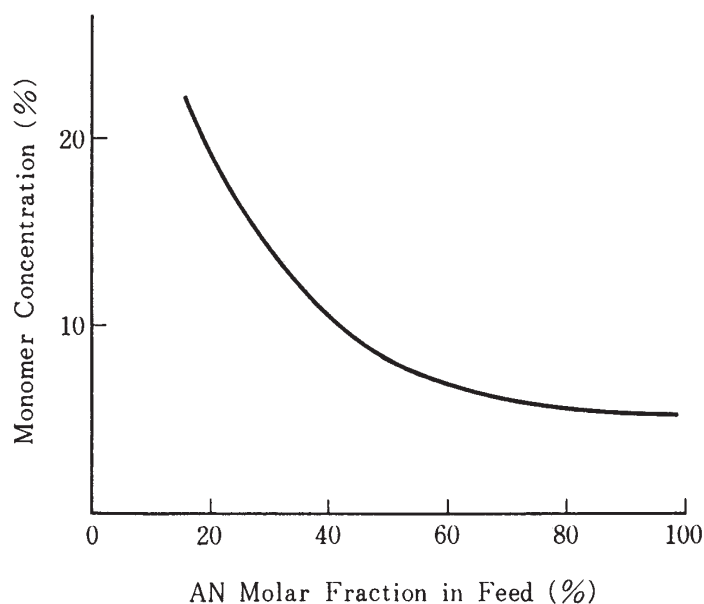


Fig. 6 Monomer concentration vs AN molar fraction in feed.

and the peak area intensities ($C(A)$) are summarized in **Table 5**. The average monomer yield in AN-FA copolymers obtained from PGC is plotted against the molar fraction in **Fig. 6**.

The AN-FA copolymers also have some non-linear relationship between the monomer yields and the molar conversion. Tsuge proposed the relationship between the amount of monomer yield ($C(A)$) and the monomer formation probability constants (K) as equation (1).

$$\begin{aligned}
 C(A) &= \frac{1}{(r_A z + 1)^2} \{r_A^2 z^2 (K_1 \cdot C_0(A)) + 2 r_A z (K_2 \cdot C_0(A)) + K_4 \cdot C_0(A)\} \\
 &= \frac{1}{(r_A z + 1)^2} \{r_A^2 z^2 K_1' + 2 r_A z K_2' + K_4'\} \quad (1)
 \end{aligned}$$

where r_A is the monomer reactivity ratio, z is initial monomer molar fraction, $C_0(A)$ is the sensitivity of A monomer at 1 mg (the peak area of the integration), K_i ($i=1-4$) are A monomer formation probability constants, $K_1' = K_1 \cdot C_0(A)$, $K_2' = K_2 \cdot C_0(A)$, $K_4' = K_4 \cdot C_0(A)$.

The relationship of monomer peak area intensity in the copolymer with the run number (R) are shown in the following equation (2).

$$R_{exp.} = 200 \cdot F_A \frac{(K_1' - K_2') \pm (K_2'^2 - K_1' \cdot K_4') + (K_1' + K_4' - 2 K_2') C(A)}{K_1' + K_4' - 2 K_2'} \quad (2)$$

FA is mole conversion of A component in a copolymer. The equation (1) and (2) for C(A) contains three unknowns (K_1', K_2', K_4'), but it is experimentally possible to determine the run number using three sets of C(A) values at least for three copolymers with different composition.

The theoretical run number from usual copolymerization theory is calculated by equation (3),

$$R_{theo.} = \frac{200 z}{r_A z^2 + 2 z + r_B} \quad (3)$$

where r_A, r_B are the monomer reactivity ratios from A, B monomer, respectively. The theoretical and experimental run numbers of AN-FA copolymers, which are calculated by eq. (2) and (3), are summarized in **Table 6**. The experimental run number is fairly compatible with the theoretical one at AN/FA=1/2. However, the positive deviations of experimental run numbers increase with the increments of acrylonitrile content in the copolymers. It is considered that there are two reasons for these results. One is as follows. As expected from the reactivity ratios of AN and FA monomer ($r_{AN}=0.2$ and $r_{FA}=0.7$), in this copolymerization, the terminal AN radical reacts to FA monomer very easily. So, in the case of feeding large molar fraction of AN monomer, this copolymer has more alternate distribution than the statistical copolymer. The other reason is that at large molar fraction of AN monomer, the product (copolymer) can not be dissolved in solvent and precipitates, i.e., the polymerization changes to heterogeneous from homogeneous polymerization. Therefore it is clear that AN-FA copolymers have more random distribution of monomer unit than AN-EA copolymers.

Table 6 Run Numbers of AN-FA Copolymers.

Molar Ratio in Feed AN-FA	$R_{theo.}$	$R_{exp.}$
1 : 2	57	61
1 : 1	69	85
2.4 : 1	73	99

4 Conclusion

The sequence distribution of copolymers were investigated by PGC. At AN-EA copolymers, the run number and average chain length of AN, EA monomer was calculated by relative yields of AN-AN, EA-EA and AN-EA dimer. In the case of the AN-FA copolymers, the scission of the long side chain took place by pyrolysis. So we could not apply the same method to these copolymers. Then the yields of AN monomer were used for the calculation of run number. These results are summarized as follows :

- (1) Average run number of AN-EA and AN-FA copolymer are 40 and 60, respectively.
- (2) The discrepancy of experimental and theoretical run number at large molar fraction of AN monomer for AN-FA copolymers is due to the heterogeneous polymerization in this range.

—Reference—

- (1) Yamamoto, Y, Tsuge, S and Takeuchi, T, *Koubunshi Kagaku*, **29**, 407 (1972)
- (2) Harwood, H J and Ritchey, W M, *J Polymer Sci*, **B 2**, 601 (1964)
- (3) Takeuchi, T and Tsuge, S, "Koubunshi no Netsubunkai Gas Chromatography", p 105 (1977), Kagakudoujin, Japan