expansion,[6] but no consistent correlation was found in this study. The methanol and formamide data appeared out of line because of the drop in a and viscosity. This, however, could be due to a special solvent effect. A consistent correlation of a with the intrinsic viscosity of fraction E(3-3) is observed. There is a rapid decrease in a found with decreasing $[\eta]_{E(3-3)}$, being lowest in formamide. If the polymer behaved like an Einstein sphere in a particular solvent, the exponent a in the Mark–Houwink equation would be zero and the intrinsic viscosity would be lower than the expanded non-free-draining coil for that polymer. Consequently, we conclude that the novolak polymer chains range from a fairly compact sphere (probably more ellipsoidal) in formamide to those behaving like normal Gaussian coils in DMF. The chains are probably acting as tightly compact structures in formamide and methanol because of the very strong intramolecular hydrogen bonding present in these compounds. In these media solvent–polymer interactions would be small, which leads to methanol and especially formamide acting as poor solvents. In the other solvents, strong intermolecular hydrogen-bonding interactions are possible, being strongest for DMF, and this allows the polymer chains to take on an expanded Gaussian form. The latter apparently approaches a model much like that expected in a Θ solvent. The NaOH data are considered explicitly in this discussion because the NaOH solution mechanism is an ionic one.

The above rationale seems like a reasonable explanation of the general trends, but does not necessarily explain exactly what is influencing the break in the Mark–Houwink curves below a molecular weight of 1000. The slope of the lower portion of the novolak curves in acetone and DMF is about 0.22, which compares to 0.24 for low molecular weight poly(propylene oxide) glycol in H_2O[5] and 0.28 in poly(ethylene oxide) glycol.[4] These are nearly the same as found for the novolaks in formamide and methanol. Although it varies with solvent and the shortness of the molecular chains, many polymers appear to have this Mark–Houwink slope behavior. It is possible that in DMF and acetone a molecular weight is reached where the polymer chains change from a random coil to a compact structure as they appear to be in formamide over a wider molecular weight range. However, if this were true, one might ask why the viscosity of low molecular weight novolaks in acetone does not show a sharp decrease instead of an increase. The viscosity upturn with decreasing molecular weight has been partly taken into account by including the importance of chain thickness relative to the mean-square chain dimensions as low molecular weight chains are approached,[13] or by considering how the smallest unit in a flexible chain of beads influences the chain viscosity.[4] Both of these methods are based on a flexible coil and hence do not seem consistent with the compact structure ideas discussed here or found in poly(propylene oxide) glycol.[6] The equivalent ellipsoid model would seem more appropriate in the low a region of the viscosity curves.

Study on the Distribution of Dyads in Acrylonitrile–Methyl Acrylate Copolymers by Pyrolysis Gas Chromatography

Yoshiyuki Yamamoto, Shin Tsuge,* and Tsugio Takeuchi

Department of Synthetic Chemistry, Faculty of Engineering,
Nagoya University, Nagoya, Japan. *Received October 4, 1971*

ABSTRACT: The distribution of dyads in acrylonitrile–methyl acrylate copolymers has been studied by means of pyrolysis gas chromatography (pgc). A cluster of dimer peaks appearing on the pyrograms has been identified by a mass spectrometer combined with pgc and interpreted in terms of the dyad distributions in the copolymers. The experimentally estimated concentrations of dyads were in fair agreement with those calculated from copolymerization theory over a wide range of composition of the copolymers.

Acrylonitrile (AN)–methyl acrylate (MA) copolymer is one of the most intractable copolymers to characterize with respect to microstructure. Although nmr can provide some information related to the monomer distribution of copolymers such as vinylidene chloride–isobutylene[1] and styrene–methyl methacrylate,[2] the spectra of the AN–MA copolymer are not sufficiently characteristic to make quantitative interpretation of the microstructures possible.

In our previous work,[3,4] pyrolysis gas chromatography (pgc) was successfully used for the first time to determine the quantitative concentration of the triad sequences in vinylidene chloride–vinyl chloride copolymers. Although some studies on the characterization of AN–MA copolymer have been reported by means of pgc, none have succeeded in obtaining quantitative data concerning the monomer distribution. Wall[5] and Shibasaki,[6,7] however, have already suggested that the boundary effects of the pyrolysis of the copolymer which will affect the formation of hybrid monomers provide good information about the monomer distribution.

In this paper, the concentrations of dyads in the copolymers have been experimentally estimated utilizing the cluster of dimer peaks appearing on the pyrograms of AN–MA copolymers by means of pgc. The identification of the dimer peaks was carried out by combining pgc directly with a mass spectrometer (ms). The observed dyad concentrations were successfully compared with those calculated from the copoly-

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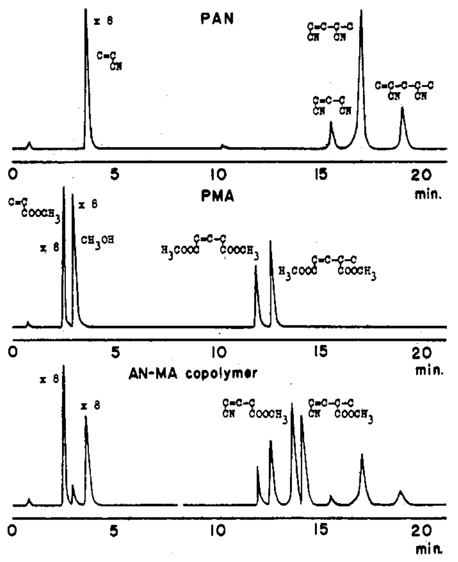


Figure 1. Typical pyrograms of polyacrylonitrile (PAN), poly(methyl acrylate) (PMA), and AN–MA copolymer (sample no. 4).

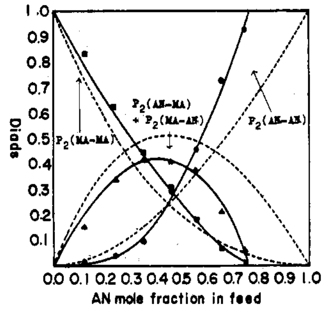


Figure 2. The concentrations of dyads in the AN–MA copolymers. Mole fraction of dyads *vs.* mole fraction of AN in monomer feed: (——) the observed curves, (-----) the theoretical curves.

TABLE I
COMPOSITION OF AN–MA COPOLYMER SAMPLE

Sample no.	AN in feed, mole fraction	AN in copolymer, mole fraction[a]
1	0.123	0.184
2	0.240	0.292
3	0.351	0.397
4	0.458	0.504
5	0.558	0.609
6	0.655	0.734
7	0.747	0.885

[a] Calculated from nitrogen content (elemental analysis)

mer theory over a wide range of composition of the copolymers.

Experimental Section

Materials. Samples of AN–MA copolymers of different composition were prepared by bulk polymerization at 50° in the presence of α,α'-azobisisobutyronitrile (AIBN). When a weight conversion of 1–3% was reached, the polymer was precipitated with methanol and purified by reprecipitation with methanol from *N,N*-dimethylformamide solution and then dried under vacuum at 50° for 48 hr.

The compositions of the prepared samples are shown in Table I. By supposing pure radical polymerization, the reactivity ratios, $r_{AN} = 1.17$ and $r_{MA} = 0.76$, were experimentally determined by the Fineman–Ross method.

Pyrolysis Gas Chromatographic Conditions. The gas chromatograph and the furnace-type pyrolyzer are the same as those described in our previous work.[3,4] The chromatographic column (2 m × 3 mm i.d.) was packed with Diasolid L (80–100 mesh) coated with PEG-6000 (10 wt %). The column temperature was programmed from 60 to 200° at the rate of 16°/min. The copolymer sample weighing about 0.5 mg was pyrolyzed in the pyrolyzer at 470° under the flow of nitrogen carrier gas.

Identification of the pyrolysis products appearing on the pyrograms was carried out by combination of the pyrolysis gas chromatograph with a mass spectrometer, Hitachi RMS-4.

Results and Discussion

Typical pyrograms of polyacrylonitrile (PAN), poly(methyl acrylate) (PMA), and AN–MA copolymer are shown in Figure 1. The main degradation products of PAN are acrylonitrile monomer and a cluster of dimers. Similarly, in the case of PMA, methyl acrylate monomer and dimers are formed. On the other hand, AN–MA copolymers yield characteristic hybrid dimers in addition to the above products.

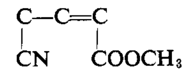
At moderately high temperature, the chain scission reaction takes place to yield macromolecular radicals which subsequently unzip into monomers, dimers, and other molecules. The total yield of dimers is approximately one order of magnitude smaller than that of the monomers with respect to the copolymer used. In the following, the relative yield of the dimers is discussed in connection with the dyad distributions in the copolymers.

Provided that the macromolecular radicals from the copolymer breakdown produce molecules with an even number of carbon atoms in the polymer chain, then the following degradation products will be formed.

macromolecular radical		monomer	dimer
——AN–AN·	⟶	AN	AN–AN
——AN–MA· ——MA–AN·	⟶	AN, MA	AN–MA
——MA–MA·	⟶	MA	MA–MA

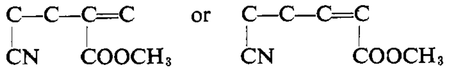
However, it is shown in Figure 2 that the resulting degradation products consist of various carbon skeletons.

For example, two kinds of hybrid dimers are observed as follows.



$$\underset{CN}{C}-C=\underset{COOCH_3}{C}$$

I



$$\underset{CN}{C}-C-\underset{COOCH_3}{C}=C \quad \text{or} \quad C-\underset{CN}{C}-C=\underset{COOCH_3}{C}$$

II

Although these hybrid dimers differ from one another in carbon number, all of them have been assigned to an AN–MA unit after making corrections for the molecular sensitivity of each component in the flame ionization detecter.[8] A similar procedure was adopted with respect to the AN–AN and MA–MA units. Therefore, the total amount of AN dimers may correspond to the concentration of the sequence of the AN–AN unit, the total amount of MA dimers also may correspond to the concentration of the sequence of the MA–MA unit, and, similarly, the total amount of hybrid dimers may correspond to the concentration of the sequence of the AN–MA unit and the MA–AN unit.

Summarizing the thermal degradation mechanisms men-

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(8) J. C. Sternberg, W. S. Gallaway, and D. T. L. Jones, "Gas Chromatography," N. Brenner, *et al.*, Ed., Academic Press, New York, N. Y., 1962, p 231.

tioned above, we obtain the following relationships between the dyads and the yields of the characteristic degradation products

$$P_2(\text{AN–AN}) = k_1 Y_{\text{AN–AN}}$$

$$P_2(\text{AN–MA}) + P_2(\text{MA–AN}) = k_2 Y_{\text{AN–MA}}$$

$$P_2(\text{MA–MA}) = k_3 Y_{\text{MA–MA}}$$

where $P_2(\ldots)$ represents the corresponding dyad concentration, k_1, k_2, and k_3 are constants, and $Y_{\text{AN–AN}}$, $Y_{\text{AN–MA}}$, and $Y_{\text{MA–MA}}$ are the observed relative yields of the dyads ($Y_{\text{AN–AN}} + Y_{\text{AN–MA}} + Y_{\text{MA–MA}} = 1$). In the actual degradation reactions of the copolymer, k_1, k_2, and k_3 would be some complicated functions of the pyrolysis temperature and the copolymer composition. However, if k_1, k_2, and k_3 are unity over the whole range of the composition with the given pyrolysis conditions, we can obtain the following simplified relationships.

$$P_2(\text{AN–AN}) = Y_{\text{AN–AN}} \tag{1}$$

$$P_2(\text{AN–MA}) + P_2(\text{MA–AN}) = Y_{\text{AN–MA}} \tag{2}$$

$$P_2(\text{MA–MA}) = Y_{\text{MA–MA}} \tag{3}$$

While applying the usual copolymerization theory (terminal model), we can obtain relationships 4, 5, and 6, corresponding to (1), (2), and (3), respectively.

$$P_2(\text{AN–AN}) = P_1(\text{AN})P_{\text{AN–AN}} = \frac{r_{\text{AN}}z}{2 + r_{\text{AN}}z + r_{\text{MA}}/z} \tag{4}$$

$$P_2(\text{AN–MA}) + P_2(\text{MA–AN}) =$$

$$P_1(\text{AN})\text{P}_{\text{AN–MA}} + P_1(\text{MA})\text{P}_{\text{MA–AN}} = \frac{2}{2 + r_{\text{AN}}z + r_{\text{MA}}/z} \tag{5}$$

$$P_2(\text{MA–MA}) = P_1(\text{MA})P_{\text{MA–MA}} = \frac{r_{\text{MA}}/z}{2 + r_{\text{AN}}z + r_{\text{MA}}/z} \tag{6}$$

Here $P_1(\ldots)$ represents the corresponding monomer concentration and $P_{\text{AN–AN}}$, for example, is the probability of AN unit followed by AN. As mentioned above, the monomer reactivity ratios $r_{\text{AN}} = 1.17$ and $r_{\text{MA}} = 0.76$ were utilized. The value of z stands for the monomer mole ratio ($F_{\text{AN}}/F_{\text{MA}}$) in the polymerization system.

The observed and calculated concentrations of dyads in the copolymer are listed in Table II. In Figure 2, the observed dyad concentrations are plotted against the mole fraction of AN in the feed $[F_{\text{AN}}/(F_{\text{AN}} + F_{\text{MA}})]$, together with the theoretical curves calculated from eq 4–6. Although the observed dyad concentrations do not always fall on the theoretical curves mainly because of the rough assumption on k_1, k_2, and k_3, they reflect fairly well the tendency of the dyad distribution over a wide range of the composition.

TABLE II

OBSERVED AND THEORETICAL CONCENTRATION OF THE DYADS IN AN–MA COPOLYMERS

Sample no.	P_2(AN–AN) Calcd	P_2(AN–AN) Obsd	P_2(AN–MA) + P_2(MA–AN) Calcd	P_2(AN–MA) + P_2(MA–AN) Obsd	P_2(MA–MA) Calcd	P_2(MA–MA) Obsd
1	0.021	0.015	0.264	0.151	0.715	0.834
2	0.077	0.039	0.419	0.340	0.504	0.621
3	0.157	0.147	0.495	0.421	0.348	0.432
4	0.254	0.291	0.514	0.407	0.232	0.302
5	0.362	0.452	0.490	0.374	0.148	0.174
6	0.480	0.722	0.433	0.209	0.087	0.069
7	0.605	0.924	0.350	0.057	0.045	0.019

TABLE III

COMPARISON OF THE AN CONTENT BEFORE AND AFTER PYROLYSIS

Sample no.	AN content, mol A[a]	AN content, mol B[b]	Conversion rate, %
1	0.091	0.184	49.5
2	0.209	0.292	71.6
3	0.358	0.397	90.2
4	0.494	0.504	98.0
5	0.639	0.609	105.0
6	0.827	0.734	112.7
7	0.953	0.885	107.7

[a] P(AN–AN) + $^1/_2P$(MA–AN). Observed data from the pyrograms. [b] In the copolymer. The same as those in Table I.

Table III shows the data which compare AN concentrations in the copolymers determined from nitrogen contents and those calculated from the observed dyad concentrations. These data suggest that the conversion rate of an AN unit in the copolymers to dimers containing AN changes as an almost monotonously increasing function of the AN concentration. The conversion rate is also good indication of the reliability of this method.

In this work, we have demonstrated a possibility of characterizing dyad distributions of copolymer by use of pgc. Further work on microstructures of the other copolymers is currently in progress.