laser radiation scattered from fluctuations in refractive index caused by interplanar twiston and splayon modes. These diffusive modes apparently tighten up upon the application of an applied field narrowing the laser line width. The critical electric field for our samples in chloroform solution occurs at 350 V/cm. The untwisting process is relatively slow (~30 min) and apparently involves two reorientation mechanisms with different time constants.

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Pyrolysis Gas Chromatographic Evaluation on Sequence Distribution of Dyads in Vinyl-Type Copolymers: Acrylonitrile–*m*-Chlorostyrene and Acrylonitrile–*p*-Chlorostyrene Copolymers

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ABSTRACT: Thermal degradation of vinyl-type copolymers which yield dimers was studied theoretically and experimentally by means of pyrolysis gas chromatography (pgc). New parameters, dimer formation probability constant, were proposed to account for the influence of boundary effects on the formation of dimers during pyrolysis of copolymers. The proposed method was successfully applied for characterizing dyad sequence distribution in acrylonitrile–*m*-chlorostyrene and acrylonitrile–*p*-chlorostyrene copolymers.

Although thermal decomposition is probably one of the oldest techniques for the chemist, it has played an important role in the development of our present knowledge of the nature and structure of high polymers. Especially, pyrolysis gas chromatography (pgc) has become an increasingly useful tool for the elucidation of the detailed structure, thermal stability and degradation kinetics of polymers. However, studies on copolymer microstructure have been relatively few, mainly because of our incomplete knowledge about the detailed processes of copolymer decomposition.

One general feature of the degradation results is that the yield of monomers, dimers, etc., from copolymer changes as a function of many factors, such as the nature of the constituent monomers, the arrangement and the distribution of the monomer units in the copolymer chain, pyrolysis temperature and atmosphere, etc. Wall[1-3] has developed a theory to relate the monomer yield from vinyl-type copolymer to the arrangement of monomer units in the polymer, introducing a concept of the boundary effect caused by the neighboring monomer units. Shibasaki[4-6] has modified Wall's concept and estimated that the boundary effect is mainly due to the influence of penultimate units on the stability of depropagating copolymer chain radicals. He applied it to acrylonitrile–styrene and methyl methacrylate–styrene copolymers. In the studies, he defined that the value of the boundary effect parameter, β, should be constant for a copolymer system at a given pyrolysis temperature. However when the penultimate effect is to be strictly applied for the degradation of copolymer, the formation of different types of depropagating polymer chain radicals should also be affected by the original neighboring monomer units. Accordingly the value of β might not always be constant, but could change as a function of monomer distribution in the polymer chain. Reported relations between the boundary effect and copolymer composition also suggest that the value of β is not necessarily constant.

In recent reports,[7-9] dyad distributions in some vinyl-type copolymers such as acrylonitrile–methyl acrylate, acrylonitrile–styrene, styrene–*m*-chlorostyrene, and styrene–*p*-chlorostyrene copolymers have been discussed on the basis of the dimer yield by means of pgc. In this work, a new theory was developed for the evaluation of dyad sequence distribution in vinyl-type copolymers applying the both-side boundary effect on the dimer yield from copolymer through pyrolysis. This theory was successfully applied for acrylonitrile–*m*-chlorostyrene (AN–*m*-CSt) and acrylonitrile–*p*-chlorostyrene (AN–*p*-CSt) copolymers.

Theory for the Formation of Dimers from Copolymers During Degradation

On thermal decomposition a copolymer composed of A and B monomer units, breaking bonds through various processes, would produce monomers (A and B), dimers (AA, AB, and BB), etc. Provided that these degradation products are free from recombination and other complicated secondary reactions, they should reflect the original microstructures to some extent.

As was discussed in earlier papers,[7-9] there should be some functionality between dyad concentration and observed relative dimer yield

Table I
Dimer Formation Probability Constants

Dyad Unit in Tetrad Section of Copolymer Chain	Dimer Formation Probability Constant	Formed Dimer
$\sim\mathrm{A\overline{AA}A}\sim$	$K(\mathrm{A\overline{AA}A})\mathrm{AA}$	AA
$\sim\mathrm{A\overline{AA}B}\sim$	$K(\mathrm{A\overline{AA}B})\mathrm{AA}$ $(= K(\mathrm{B\overline{AA}A})\mathrm{AA})$	AA
$\sim\mathrm{B\overline{AA}B}\sim$	$K(\mathrm{B\overline{AA}B})\mathrm{AA}$	AA
$\sim\mathrm{A\overline{AB}A}\sim$	$K(\mathrm{A\overline{AB}A})\mathrm{AB}$	AB
$\sim\mathrm{A\overline{AB}B}\sim$	$K(\mathrm{A\overline{AB}B})\mathrm{AB}$	AB
$\sim\mathrm{B\overline{AB}A}\sim$	$K(\mathrm{B\overline{AB}A})\mathrm{AB}$	AB
$\sim\mathrm{B\overline{AB}B}\sim$	$K(\mathrm{B\overline{AB}B}(\mathrm{AB}$	AB
$\sim\mathrm{A\overline{BB}A}\sim$	$K(\mathrm{A\overline{BB}A})\mathrm{BB}$	BB
$\sim\mathrm{A\overline{BB}B}\sim$	$K(\mathrm{A\overline{BB}B})\mathrm{BB}$ $(= K(\mathrm{B\overline{BB}A})\mathrm{BB})$	BB
$\sim\mathrm{B\overline{BB}B}\sim$	$K(\mathrm{B\overline{BB}B})\mathrm{BB}$	BB

Table II
Composition of the Copolymer Samples

Sample	AN in Feed mol Fraction	AN in Copolymer[a] mol Fraction
	AN–m-CSt Copolymers	
1	0.094	0.264
2	0.190	0.308
3	0.344	0.396
4	0.469	0.439
5	0.634	0.505
6	0.757	0.537
7	0.864	0.610
8	0.954	0.739
	AN–p-CSt Copolymers	
a	0.094	0.254
b	0.220	0.306
c	0.315	0.359
d	0.411	0.404
e	0.573	0.460
f	0.712	0.506
g	0.808	0.547
h	0.897	0.613
i	0.959	0.730

[a] Calculated from nitrogen content by elemental analysis.

Table III
Copolymerization Reactivity Ratio

Copolymer	Reactivity Ratio[a]	
AN–m-CSt	$r_A = 0.099$	$r_m = 0.297$
AN–p-CSt	$r_A' = 0.075$	$r_p = 0.388$

[a] $r_A(r_A')$, r_m and r_p denote the monomer reactivity ratios for acrylonitrile, *m*-chlorostyrene, and *p*-chlorostyrene, respectively.

$$P_2(\mathrm{AA}) = k_1Y_2(\mathrm{AA}) \tag{1}$$

$$P_2(\mathrm{AB}) + P_2(\mathrm{BA}) = (2P_2(\mathrm{AB})) = k_2Y_2(\mathrm{AB}) \tag{2}$$

$$P_2(\mathrm{BB}) = k_3Y_2(\mathrm{BB}) \tag{3}$$

where $P_2(\cdots)$ represents dyad concentration in the copolymer, $Y_2(\mathrm{AA})$, $Y_2(\mathrm{AB})$, and $Y_2(\mathrm{BB})$ are the observed relative dimer yield ($Y_2(\mathrm{AA}) + Y_2(\mathrm{AB}) + Y_2(\mathrm{BB}) = 1$), and k_1, k_2, and k_3 are correction parameters. The values of the parameters need not be constant through its entire range of copolymer composition, even for a given copolymer system, but could vary depending on the dyad arrangement and concentration.

In the following, the relations between the regenerated dimers appearing on the pyrogram and the dyad sequence distribution in the copolymer are discussed in terms of the influence of both units that are neighbors to a given dyad on the tendency of that dyad to be observed as a dimer fragment under a given set of degradation conditions (temperature, atmosphere, etc.). For example, the AA dimer can be liberated from the following different surroundings in the copolymer chain: $\sim\mathrm{A\overline{AA}A}\sim$, $\sim\mathrm{B\overline{AA}A}\sim$, and $\sim\mathrm{B\overline{AA}B}\sim$. Of course, the central dyad $\overline{\mathrm{AA}}$ unit can also participate to yield degradation products other than dimer AA, and, moreover, the formation probability of AA from the three different tetrad sections in the chain should be different from each other. Here the formation probability constants for dimer AA are defined $K(\mathrm{A\overline{AA}A})\mathrm{AA}$, $K(\mathrm{B\overline{AA}A})\mathrm{AA}$, and $K(\mathrm{B\overline{AA}B})\mathrm{AA}$ from $\sim\mathrm{A\overline{AA}A}\sim$, $\sim\mathrm{B\overline{AA}A}\sim$, and $\sim\mathrm{B\overline{AA}B}\sim$, respectively. The other probability constants are defined similarly and are summarized in Table I. From the definitions in Table I, we can obtain the following equations, corresponding to eq 1–3.

$$\begin{aligned} Y_2(\mathrm{AA}) &= P_4(\mathrm{AAAA})K(\mathrm{A\overline{AA}A})\mathrm{AA} + 2P_4(\mathrm{AAAB})K(\mathrm{A\overline{AA}B})\mathrm{AA} + P_4(\mathrm{BAAB})K(\mathrm{B\overline{AA}B})\mathrm{AA} \\ &= P_2(\mathrm{AA})\{P_{\mathrm{AA}}{}^2K(\mathrm{A\overline{AA}A})\mathrm{AA} + 2P_{\mathrm{AA}}P_{\mathrm{AB}}K(\mathrm{A\overline{AA}B})\mathrm{AA} + P_{\mathrm{AB}}{}^2K(\mathrm{B\overline{AA}B})\mathrm{AA}\} \end{aligned} \tag{4}$$

$$\begin{aligned} Y_2(\mathrm{AB}) &= P_4(\mathrm{AABA})K(\mathrm{A\overline{AB}A})\mathrm{AB} + P_4(\mathrm{AABB})K(\mathrm{A\overline{AB}B})\mathrm{AB} + P_4(\mathrm{BABA})K(\mathrm{B\overline{AB}A})\mathrm{AB} + P_4(\mathrm{BABB})K(\mathrm{B\overline{AB}B})\mathrm{AB} \\ &= P_2(\mathrm{AB})\{P_{\mathrm{AA}}P_{\mathrm{BA}}K(\mathrm{A\overline{AB}A})\mathrm{AB} + P_{\mathrm{AA}}P_{\mathrm{BB}}K(\mathrm{A\overline{AB}B})\mathrm{AB} + P_{\mathrm{AB}}P_{\mathrm{BA}}K(\mathrm{B\overline{AB}A})\mathrm{AB} + P_{\mathrm{AB}}P_{\mathrm{BB}}K(\mathrm{B\overline{AB}B})\mathrm{AB}\} \end{aligned} \tag{5}$$

$$\begin{aligned} Y_2(\mathrm{BB}) &= P_4(\mathrm{ABBA})K(\mathrm{A\overline{BB}A})\mathrm{BB} + 2P_4(\mathrm{ABBB})K(\mathrm{A\overline{BB}B})\mathrm{BB} + P_4(\mathrm{BBBB})K(\mathrm{B\overline{BB}B})\mathrm{BB} \\ &= P_2(\mathrm{BB})\{P_{\mathrm{BA}}{}^2K(\mathrm{A\overline{BB}A})\mathrm{BB} + 2P_{\mathrm{BA}}P_{\mathrm{BB}}K(\mathrm{A\overline{BB}B})\mathrm{BB} + P_{\mathrm{BB}}{}^2K(\mathrm{B\overline{BB}B})\mathrm{BB}\} \end{aligned} \tag{6}$$

where $P_4(\cdots\cdot)$ represents a tetrad concentration of the copolymer, and P_{AB}, for example, is the probability of an A unit followed by a B unit in the copolymer. These values can be expressed in terms of monomer reactivity ratios (r_A and r_B) and initial monomer mole feed ratios, z ($= F_A/F_B$) for copolymerization. Combining eq 1–6 the correction parameters, k_1, k_2, and k_3 are expressed as follows

$$k_1 = \frac{(r_Az + 1)^2}{Az^2 + Bz + C} \tag{7}$$

where $A = r_A{}^2K(\mathrm{A\overline{AA}A})\mathrm{AA}$, $B = 2r_AK(\mathrm{A\overline{AA}B})\mathrm{AA}$, and $C = K(\mathrm{B\overline{AA}B})\mathrm{AA}$.

$$k_2 = \frac{(1/2)(r_Az + 1)(z + r_B)}{Dz^2 + Ez + F} \tag{8}$$

where $D = r_AK(\mathrm{A\overline{AB}A})\mathrm{AB}$, $E = K(\mathrm{B\overline{AB}A})\mathrm{AB} + r_Ar_B\cdot K(\mathrm{A\overline{AB}B})\mathrm{AB}$, and $F = r_BK(\mathrm{B\overline{AB}B})\mathrm{AB}$.

$$k_3 = \frac{(z + r_B)^2}{Gz^2 + Hz + I} \tag{9}$$

where $G = K(\mathrm{A\overline{BB}A})\mathrm{BB}$, $H = 2r_BK(\mathrm{A\overline{BB}B})\mathrm{BB}$, and $I = r_B{}^2K(\mathrm{B\overline{BB}B})\mathrm{BB}$.

As each equation for k_1, k_2, and k_3 contains three unknowns, it is experimentally possible to determine the

Table IV
Relative Yield of Monomer and Dimer from Copolymer Samples

Sample	Monomers	Dimers	Other Products
	Rel Yields from Samples[a]		
	AN-m-CSt Copolymers		
1	0.532	0.114	0.354
2	0.538	0.125	0.337
3	0.517	0.137	0.346
4	0.502	0.138	0.360
5	0.497	0.136	0.367
6	0.443	0.139	0.418
7	0.328	0.115	0.557
8	0.244	0.112	0.644
	AN-p-CSt Copolymers		
a	0.534	0.114	0.352
b	0.481	0.093	0.426
c	0.467	0.099	0.434
d	0.463	0.117	0.420
e	0.439	0.124	0.437
f	0.450	0.122	0.428
g	0.401	0.115	0.484
h	0.376	0.117	0.507
i	0.189	0.101	0.710
	Homopolymers		
PAN	0.076	0.109	0.815
P-m-CSt	0.644	0.068	0.288
P-p-CSt	0.663	0.075	0.262

[a] Relative yields are defined as the amount of monomer (or dimers) *vs.* sample weight by calibration of standard monomer samples.

dimer formation probability constants using three sets of k_1, k_2, and k_3 values obtained at least for three copolymers with different composition. Once the probability constants are decided for a copolymer system, we can calculate any sequence distribution of dyad in the copolymer chain from the observed relative dimer yield.

Experimental Section

Materials. AN-*m*-CSt and AN-*p*-CSt copolymers and the associated homopolymers were prepared by a free-radical bulk polymerization of the monomers using α,α'-azoisobutylonitrile (AIBN) as initiator at 50°. When a weight conversion of 2–6% was reached the polymer was precipitated with methanol and purified by reprecipitation with methanol from acetone solution, and then dried under vacuum at 60° for 48 hr. The composition of the copolymers was determined by elemental analysis, and listed in Table II. Assuming pure radical copolymerization, the monomer reactivity ratios for both copolymer systems were experimentally determined by the Fineman–Ross method; the results are shown in Table III.

Pyrolysis Gas Chromatographic Conditions and Peak Identification. A furnace-type pyrolyzer, Hitachi KP-1, was used to decompose the polymers. It was directly attached to the inlet port of a Hitachi Model 063 gas chromatograph with dual-flame ionization detectors. Samples weighed by a Cahn Electrobalance Model G-2, ranging from 300 to 500 μg, were pyrolyzed at 530° under a flow of carrier gas (N_2). The separating column, 1-m stainless tubing (3-mm i.d.) packed with 10% FFAP (free fatty acid polyester) on 80–100 mesh Uniport B, was programed between 100 and 290° at a rate of 10°C/min. Identification of the degradation products appearing on pyrograms was performed by connecting the pyrolysis gas chromatograph with a mass spectrometer, Hitachi RMS-4. The exact position of double bond for some identified dimers could not be determined. However, this introduced no difficulties in the calculation of dyad concentrations since isomers differing only in double-bond position should have almost the same sensitivity for the flame ionization detectors.

Results and Discussion

Figures 1 and 2 show the typical pyrograms of polyacrylonitrile (PAN), poly(*m*-chlorostyrene) (P-*m*-CSt) and AN-*m*-CSt copolymer, and poly(*p*-chlorostyrene) (P-*p*-CSt) and AN-*p*-CSt copolymer, respectively, at the pyrolysis temperature of 530°. During thermal decomposition, vinyl-type copolymers decompose into monomers, dimers, and other products. Some of the other products cannot be seen on the pyrogram, being trapped by the separation column because of their low volatility and/or remaining as residue in the pyrolyzer. In the case of the copolymer used, a portion of the other products were possible to separate as trimers which were not shown in Figures 1 and 2 because of their long retention time and small quantities. The main degradation products from

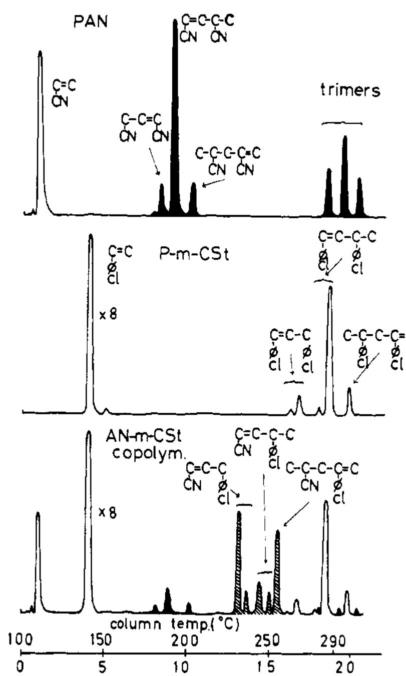


Figure 1. Typical pyrograms of PAN, P-*m*-CSt, and AN-*m*-CSt copolymer (sample 4).

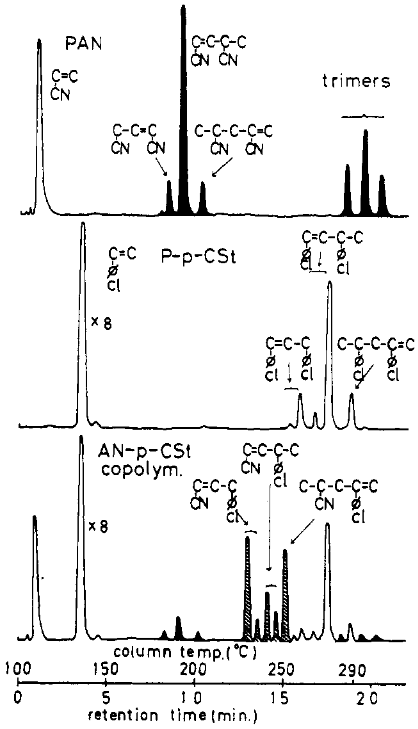


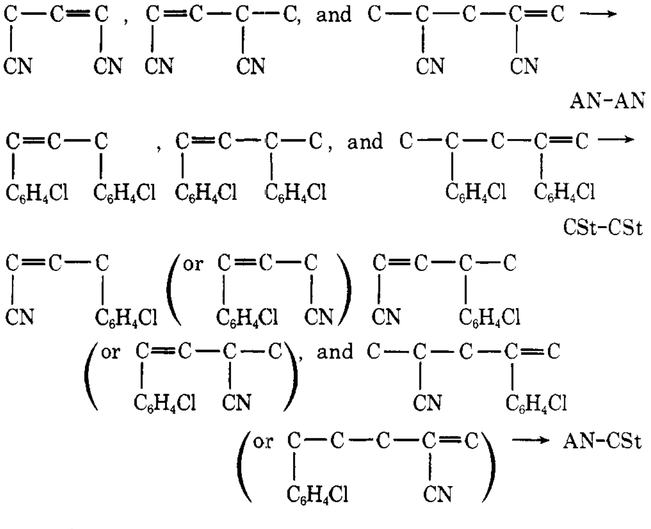
Figure 2. Typical pyrograms of PAN, P-*p*-CSt, and AN-*p*-CSt copolymer (sample e).

Table V
Observed and Theoretical Dyad Concentrations

Sample	Y_2(AA) Obsd	P_2(AA)	k_1 Obsd	Y_2(AB) Obsd	P_2(AB)	k_2 Obsd	Y_2(BB) Obsd	P_2(BB)	k_3 Obsd
				AN-m-CSt Copolymers					
1	0.031	0.002		0.349	0.411		0.620	0.587	0.947
2	0.065	0.007		0.478	0.608		0.457	0.385	0.842
3	0.112	0.020		0.577	0.764		0.311	0.216	0.695
4	0.164	0.036		0.615	0.825	1.341	0.221	0.139	
5	0.224	0.073		0.621	0.854	1.375	0.155	0.073	
6	0.275	0.128	0.465	0.615	0.832	1.354	0.110	0.040	
7	0.395	0.235	0.595	0.543	0.749		0.062	0.018	
8	0.538	0.483	0.898	0.447	0.513		0.015	0.004	
				AN-p-CSt Copolymers					
a	0.012	0.001		0.340	0.348		0.648	0.651	1.005
b	0.046	0.006		0.531	0.589		0.423	0.405	0.957
c	0.068	0.012		0.603	0.695		0.329	0.293	0.891
d	0.120	0.020		0.629	0.767	1.219	0.251	0.213	
e	0.128	0.042		0.678	0.837	1.235	0.194	0.121	
f	0.195	0.079		0.681	0.854	1.254	0.124	0.067	
g	0.272	0.131	0.482	0.646	0.831		0.082	0.038	
h	0.411	0.242	0.589	0.554	0.741		0.035	0.017	
i	0.583	0.465	0.798	0.407	0.530		0.010	0.005	

PAN, P-*m*-CSt, and P-*p*-CSt are monomers and dimers, while the copolymers yield characteristic hybrid dimers in addition to the above products. Table IV shows the relative yields of monomers, dimers, and other products from the homopolymers and copolymers. The amounts of other products were calculated by subtracting the absolute yields of monomers and dimers from the quantity of decomposed polymer sample. The yield of monomers decreases with the rise of acrylonitrile content in the copolymers, which also reflect the boundary effect.[4-6] However, the yields of dimers are nearly constant throughout the copolymer composition range studied. In this case, the boundary effect should be seen in the relative dimer yield between Y_2(AA), Y_2(AB), and Y_2(BB). Therefore, in the following, the relative dimer yield will be discussed.

As shown in Figures 1 and 2, the resulting dimers consist of various carbon skeltons. In the following calculation, all associating dimer peaks were assigned to one dyad. For example, three kinds of dimers which contain two -C(CN)- units were assigned to the AN-AN dimer after making correction for the molar sensitivity of each component in the flame ionization detector.[10] Similarly, the other dimer peaks were assigned to other dyads as follows



$$\underset{\mathrm{CN}}{\mathrm{C}}-\mathrm{C}=\underset{\mathrm{CN}}{\mathrm{C}},\ \underset{\mathrm{CN}}{\mathrm{C}}=\mathrm{C}-\mathrm{C}-\underset{\mathrm{CN}}{\mathrm{C}},\ \text{and}\ \mathrm{C}-\underset{\mathrm{CN}}{\mathrm{C}}-\mathrm{C}-\underset{\mathrm{CN}}{\mathrm{C}}=\mathrm{C} \longrightarrow \text{AN-AN}$$

$$\underset{\mathrm{C_6H_4Cl}}{\mathrm{C}}=\mathrm{C}-\underset{\mathrm{C_6H_4Cl}}{\mathrm{C}},\ \underset{\mathrm{C_6H_4Cl}}{\mathrm{C}}=\mathrm{C}-\mathrm{C}-\underset{\mathrm{C_6H_4Cl}}{\mathrm{C}},\ \text{and}\ \mathrm{C}-\underset{\mathrm{C_6H_4Cl}}{\mathrm{C}}-\mathrm{C}-\underset{\mathrm{C_6H_4Cl}}{\mathrm{C}}=\mathrm{C} \longrightarrow \text{CSt-CSt}$$

$$\underset{\mathrm{CN}}{\mathrm{C}}=\mathrm{C}-\underset{\mathrm{C_6H_4Cl}}{\mathrm{C}}\left(\text{or}\ \underset{\mathrm{C_6H_4Cl}}{\mathrm{C}}=\mathrm{C}-\underset{\mathrm{CN}}{\mathrm{C}}\right)\ \underset{\mathrm{CN}}{\mathrm{C}}=\mathrm{C}-\mathrm{C}-\underset{\mathrm{C_6H_4Cl}}{\mathrm{C}}\left(\text{or}\ \underset{\mathrm{C_6H_4Cl}}{\mathrm{C}}=\mathrm{C}-\mathrm{C}-\underset{\mathrm{CN}}{\mathrm{C}}\right),\ \text{and}\ \mathrm{C}-\underset{\mathrm{CN}}{\mathrm{C}}-\mathrm{C}-\underset{\mathrm{C_6H_4Cl}}{\mathrm{C}}=\mathrm{C}\left(\text{or}\ \mathrm{C}-\underset{\mathrm{C_6H_4Cl}}{\mathrm{C}}-\mathrm{C}-\underset{\mathrm{CN}}{\mathrm{C}}=\mathrm{C}\right) \longrightarrow \text{AN-CSt}$$

Applying the usual copolymerization theory (terminal model), we can obtain relationships 10–12, corresponding to eq 1–3

Table VI
Determined Dimer Formation Probability Constant for AN–*m*-CSt and AN–*p*-CSt Copolymer Systems

Dimer Formation Probability Constants	AN–*m*-CSt[a] Copolym	AN–*p*-CSt[b] Copolym
$K(\mathrm{A\overline{AA}A})\mathrm{AA}$	0.888	0.907
$K(\mathrm{A\overline{AA}B})\mathrm{AA}$	0.799	1.11
$K(\mathrm{B\overline{AA}B})\mathrm{AA}$	3.11	2.80
$K(\mathrm{A\overline{AB}A})\mathrm{AB}$	0.516	0.399
$K(\mathrm{B\overline{AB}A}(\mathrm{AB},$ $K(\mathrm{A\overline{AB}B})\mathrm{AB}$[c]	0.311	0.405
$K(\mathrm{B\overline{AB}B})\mathrm{AB}$	0.528	0.427
$K(\mathrm{A\overline{BB}A})\mathrm{BB}$	2.19	1.75
$K(\mathrm{A\overline{BB}B})\mathrm{BB}$	0.891	0.779
$K(\mathrm{B\overline{BB}B})\mathrm{BB}$	1.04	1.06

[a] A, acrylonitrile unit; B, *m*-chlorostyrene unit. [b] A, acrylonitrile unit; B, *p*-chlorostyrene unit. [c] These values were calculated by assuming $K(\mathrm{B\overline{AB}A})\mathrm{AB} = K(\mathrm{A\overline{AB}B})\mathrm{AB}$.

$$P_2(\mathrm{AA}) = P_1(\mathrm{A})P_{\mathrm{AA}} = r_{\mathrm{A}}z/(2 + r_{\mathrm{A}}z + r_{\mathrm{B}}/z) \quad (10)$$

$$P_2(\mathrm{AB}) + P_2(\mathrm{BA}) = P_1(\mathrm{A})P_{\mathrm{AB}} + P_1(\mathrm{B})P_{\mathrm{BA}} = 2/(2 + r_{\mathrm{A}}z + r_{\mathrm{B}}/z) \quad (11)$$

$$P_2(\mathrm{BB}) = P_1(\mathrm{B})P_{\mathrm{BB}} = r_{\mathrm{B}}/z/(2 + r_{\mathrm{A}}z + r_{\mathrm{B}}/z) \quad (12)$$

where $P_1(\cdot)$ represents monomer concentration in the polymer. The observed and theoretical concentrations of dyad in the copolymers are presented in Table V together with the three sets of the correction parameters, k_1, k_2, and k_3 used for the calculation of the dimer formation probability constants by solving three sets of simultaneous equations which were derived from eq 7–9. The determined values of the constants are listed in Table VI. It is very interesting to notice that the probability for the formation of homodimers such as AA and BB for both copolymer systems are enhanced about two to three times when the associated dyads in the copolymer chains are neighbored by the counter monomer units at both sides. On the other hand, the probability for the formation of hybrid dimers are relatively low and almost constant regardless of their neighboring monomer units. Once these dimer formation probability constants are determined, we can calculate any dyad concentration, $P_2(\cdot\cdot)$ from eq 4–6 using the observed relative dimer yields from the copoly-

Table VII
Calculated Dyad Concentration

Sample	Y_2(AA) Obsd	k_1 Calcd	P_2(AA) Calcd	Y_2(AB) Obsd	k_2 Calcd	P_2(AB) Calcd	Y_2(BB) Obsd	k_3 Calcd	P_2(BB) Calcd
				AN–*m*-CSt Copolymers					
1	0.031	0.327	0.010	0.349	1.063	0.371	0.620	(0.947)	0.587
2	0.065	0.333	0.022	0.478	1.160	0.554	0.457	(0.842)	0.385
3	0.112	0.347	0.039	0.577	1.277	0.737	0.311	(0.695)	0.216
4	0.164	0.364	0.060	0.615	(1.341)	0.825	0.221	0.615	0.136
5	0.224	0.403	0.090	0.621	(1.375)	0.854	0.155	0.543	0.084
6	0.275	(0.465)[a]	0.128	0.615	(1.354)	0.833	0.110	0.507	0.056
7	0.395	(0.595)	0.235	0.543	1.274	0.692	0.062	0.482	0.036
8	0.538	(0.898)	0.483	0.447	1.126	0.503	0.015	0.465	0.007
				AN–*p*-CSt Copolymers					
a	0.012	0.361	0.004	0.340	1.184	0.403	0.648	(1.005)	0.651
b	0.046	0.367	0.017	0.531	1.199	0.629	0.423	(0.957)	0.405
c	0.068	0.372	0.025	0.603	1.209	0.729	0.329	(0.891)	0.293
d	0.120	0.380	0.046	0.629	(1.219)	0.767	0.251	0.823	0.207
e	0.128	0.400	0.051	0.678	(1.235)	0.837	0.194	0.727	0.141
f	0.195	0.433	0.084	0.681	(1.254)	0.854	0.124	0.663	0.082
g	0.272	(0.482)	0.131	0.646	1.276	0.824	0.082	0.628	0.051
h	0.411	(0.589)	0.242	0.554	1.313	0.727	0.035	0.600	0.021
i	0.583	(0.798)	0.465	0.407	1.375	0.560	0.010	0.582	0.006

[a] Value in parentheses are observed ones which are used to calculate the dimer formation probability constants.

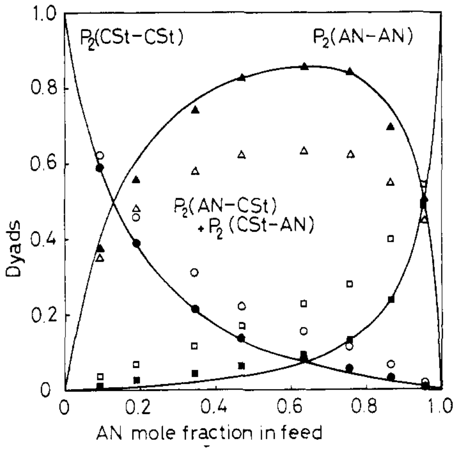


Figure 3. The concentration of dyads in the AN-*m*-CSt copolymers: (○, △, □) observed $Y_2(\cdot\cdot)$; (○, ▲, ■) calculated $P_2(\cdot\cdot)$ from the proposed theory using observed $Y_2(\cdot\cdot)$; (——) copolymerization theory $P_2(\cdot\cdot)$.

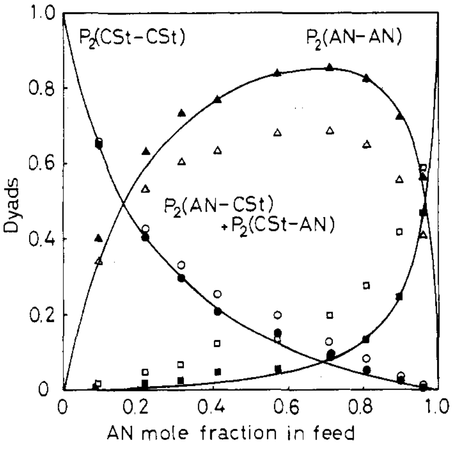


Figure 4. The concentration of dyads in the AN-*p*-CSt copolymers: (○, △, □) observed $Y_2(\cdot\cdot)$; (●, ▲, ■) calculated $P_2(\cdot\cdot)$ from the proposed theory using observed $Y_2(\cdot\cdot)$; (——) copolymerization theory $P_2(\cdot\cdot)$.

mers. The calculated dyad concentrations are shown in Table VII together with the observed relative dimer yield and the calculated correction parameters which are obtained using eq 7-9. As was discussed in an earlier paragraph, the correction factors, k_1, k_2, and k_3 in eq 1-3 are not unit constants for the entire copolymer composition, but vary as a function of monomer distribution and the boundary effect.

Figures 3 and 4 show the comparison of the observed dimer yields and the calculated dyad concentrations plotted against the relative monomer feeds for copolymerization, together with theoretical curves from copolymerization theory. As can be seen in these figures, the excellent agreement of the calculated dyad concentrations with theoretical curves would support the validity of the assumptions implicit in this method.

In this work, the proposed theory for the estimation of dyad concentrations in copolymers by pgc was examined using AN-*m*-CSt and AN-*p*-CSt copolymer systems. The same technique to characterize sequence distribution would also be applicable to the other vinyl-type copolymers from which dimer peaks are observed on the pyrograms. As shown in Table VI for AN-*m*-CSt and AN-*p*-CSt copolymer systems, it is experimentally possible using this method to evaluate the boundary effect for the formation of dimers from vinyl-type copolymers in terms of the formation probability constant. It is also possible to derive basically the same type of relationship for the formation of monomers from copolymer chains considering the both-side boundary effect. Further work on characterization of the copolymer microstructure and thermal behavior by means of pgc is currently in progress.

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