Table II
Polyacrylonitrile Heated for Various Times at 145°

Heating time, hr	C	H	N	O^a	Total
	%				
Calcd	67.92	5.66	26.42	...	100.0
0	67.92	5.66	25.97	0.6	100.11
24	67.58	5.70	25.86	0.72	99.86
48	67.51	5.65	25.50	1.04	99.70

^{a} Determined analytically.

4. It had been observed that the elemental analysis becomes increasingly incomplete with increasing coloration.[2a,3,38,39] This was confirmed in this laboratory, as shown in Table II, where the oxygen content of heated samples increases with time. This is explained by the formation of polynitrones.[10]

5. The hitherto unexplained fluorescence is caused by the presence of ketonitrile groups in the polymer.

Acknowledgment. We wish to thank Miss M. W. Huffman and Mr. D. C. Westall for experimental assistance.

(38) L. L. Bircumshaw, F. M. Taylor, and D. H. Whiffen, *J. Chem. Soc.*, 931 (1954).

(39) J. P. Kennedy and C. M. Fontana, *J. Polymer Sci.*, **39**, 501 (1959).

The Ultraviolet Degradation of Terpolymer Scissioning Systems

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Received September 27, 1967

ABSTRACT: A mathematical model has been developed to describe the uv degradation of terpolymer scissioning systems. Nearest neighbor and anomalous link (*e.g.*, head-to-head or branching) effects have been ignored in order to preserve simplicity and analytical tractability. Equations relating the fraction of various linkages and of each component in terms of reactivity ratios and monomer feed fractions are presented. A method of estimating individual scissioning constants from terpolymer experimental data is presented and the significance of the estimates is discussed. Suitable experimental designs are discussed and the simplex lattice design is suggested. Variance contours for variations on this design are presented.

The deleterious effect of ultraviolet radiation on polymers is one of the main problems barring these materials from many applications. The systematic study of uv degradation is therefore a project of considerable academic and industrial interest.

One area, in particular, that has generated a substantial amount of work is the development of a quantitative theory of uv degradation.

Previous work[1-4] has demonstrated the applicability of high-energy radiation theory to uv degradation systems with suitable modification for attenuation (film thickness)[5-7] and wavelength effects[8] (activation spectra). A theory of copolymer degradation[9] has led to characterization of polymer systems.

This paper extends previous work[9] to the scissioning behavior of terpolymer systems.

For scissioning systems a variable of fundamental importance is the number of scissions per molecule (*S*). On the assumption of a random scission mechanism this is given by eq 1, where $\bar{k}$ = over-all scissioning constant scissions/mer time^{-1}, P_0 = degree of polymerization, and t = exposure time.

$$S = \bar{k}P_0t \qquad (1)$$

Copolymers contain linkages of various types, each with a given kinetic constant for degradation. (In a copolymer of monomers A and B at least three types, A–A, A–B, and B–B are present.) It can be shown that when $\bar{k}t \ll 1$, the observed kinetic constant for degradation is the linear sum of inter-mer scission constants (*e.g.*, k_{aa}, k_{bb}, k_{ab}), each weighted by the frequency of occurrence in the copolymer (f_{aa}, f_{bb}, f_{ab}). In order to describe the degradation system it is first necessary to calculate (or measure) these linkage fractions, second to estimate and generate confidence intervals for scission constants for various linkages, and last to test the model for fit. The following discussion is divided into five sections: (I) calculation of inter-mer linkage fractions, (II) a description of the variation of the average kinetic constant with composition, (III) estimation and testing of inter-mer scission constants for the model, (IV) comments on experimental design, and (V) critique of the model.

I. Calculation of Inter-Mer Linkage Fractions

In a terpolymer of monomers A, B, and C, there are six linkages of concern, f_{aa}, f_{ab}, f_{ac}, f_{bb}, f_{bc}, and f_{cc}. The various amounts of each linkage in a terpolymer

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(1) A. Charlesby and D. K. Thomas, *Proc. Roy. Soc.* (London), **A269**, 104 (1962).

(2) C. V. Stephenson, *et al.*, *J. Polymer Sci.*, **55**, 451, 465, 477 (1961); **A1**, 2741 (1963).

(3) L. D. Maxim and C. H. Kuist, *Off. Dig., Federation Soc. Paint Technol.*, **36**, 723 (1964).

(4) H. Jacobs and R. Steele, *J. Appl. Polymer Sci.*, **3**, 239 (1960).

(5) A. R. Schultz, *J. Chem. Phys.*, **29**, 200 (1958); *J. Phys. Chem.*, **65**, 967 (1961).

(6) H. H. G. Jellinek, *J. Polymer Sci.*, **62**, 281 (1962).

(7) A. R. Schultz, *J. Appl. Polymer Sci.*, **10**, 353 (1966).

(8) R. C. Hirt, *et al.*, *J. Opt. Soc. Amer.*, **50**, 706 (1960).

(9) C. H. Kuist and L. D. Maxim, *Polymer*, **6**, 523 (1965).

depends upon the concentrations of monomers in the feed and the reactivity ratios. Analytical expressions for these fractions can be derived if the following simplifying assumptions are made: (1) the reaction is stopped at low conversion so that the actual fraction of each type of linkage approaches the instantaneous sequence ratio, (2) the effect of penultimate and antepenultimate units is negligible, (3) the steady-state assumption is valid, and (4) all linkages are head to tail and negligible branching occurs.

Table I summarizes the kinetic processes taking place in the terpolymerization of monomers A, B, and C. For a system of m monomers there are m^2 propagation steps to be considered. Numerical values are chosen for propagation constant subscripts to avoid confusion with scission constant nomenclature. The probability of finding an A–A linkage (P_{aa}) is simply the ratio of the A–A forming rate to the total propagation rate. Denoting the sum of rates ($k_{11}(m_a\cdot)(M_a) + k_{12}(m_a\cdot)(M_b) + k_{13}(m_a\cdot)(M_c) + k_{21}(m_b\cdot)(M_a)$, etc.) by B, then

$$P_{aa} = \frac{k_{11}(m_a\cdot)(M_a)}{B} \tag{2}$$

Similarly

$$P_{bb} = \frac{k_{22}(m_b\cdot)(M_b)}{B} \tag{3}$$

$$P_{cc} = \frac{k_{33}(m_c\cdot)(M_c)}{B} \tag{4}$$

$$P_{ab} = \frac{k_{12}(m_a\cdot)(M_b) + k_{21}(m_b\cdot)(M_a)}{B} \tag{5}$$

$$P_{ac} = \frac{k_{13}(m_a\cdot)(M_c) + k_{31}(m_c\cdot)(M_a)}{B} \tag{6}$$

$$P_{bc} = \frac{k_{23}(m_b\cdot)(M_c) + k_{32}(m_c\cdot)(M_b)}{B} \tag{7}$$

The relation between radical concentrations ($m_i\cdot$) and monomer feed concentrations (M_j) can be obtained from the steady-state equations[10]

$$k_{11}(m_a\cdot)(M_a) + k_{21}(m_b\cdot)(M_a) + k_{31}(m_c\cdot)(M_a) = k_{11}(m_a\cdot)(M_a) + k_{12}(m_a\cdot)(M_b) + k_{13}(m_a\cdot)(M_c) \tag{8}$$

$$k_{12}(m_a\cdot)(M_b) + k_{22}(m_b\cdot)(M_b) + k_{32}(m_c\cdot)(M_b) = k_{21}(m_b\cdot)(M_a) + k_{22}(m_b\cdot)(M_b) + k_{23}(m_b\cdot)(M_c) \tag{9}$$

$$k_{13}(m_a\cdot)(M_c) + k_{23}(m_b\cdot)(M_c) + k_{33}(m_c\cdot)(M_c) = k_{31}(m_c\cdot)(M_a) + k_{32}(m_c\cdot)(M_b) + k_{33}(m_c\cdot)(M_c) \tag{10}$$

These simplify to ratios given in eq 11–13.

$$\frac{m_b\cdot}{m_a\cdot} = \frac{M_b[k_{12}k_{31}M_a + k_{12}k_{32}M_b + k_{13}k_{32}M_c]}{M_a[k_{32}k_{21}M_b + k_{21}k_{31}M_a + k_{23}k_{31}M_c]} \tag{11}$$

$$\frac{m_c\cdot}{m_a\cdot} = \frac{M_c[k_{13}k_{21}M_a + k_{12}k_{23}M_b + k_{13}k_{23}M_c]}{M_a[k_{21}k_{31}M_a + k_{32}k_{21}M_b + k_{23}k_{31}M_c]} \tag{12}$$

$$\frac{m_c\cdot}{m_b\cdot} = \frac{M_c[k_{13}k_{21}M_a + k_{12}k_{23}M_b + k_{13}k_{23}M_c]}{M_b[k_{12}k_{31}M_a + k_{12}k_{32}M_b + k_{13}k_{32}M_c]} \tag{13}$$

TABLE I

Growing chain	Adding monomer	Rate of process	Reaction product
$—m_a\cdot$	M_a	$k_{11}(m_a\cdot)(M_a)$	$—m_am_a\cdot$
$—m_a\cdot$	M_b	$k_{12}(m_a\cdot)(M_b)$	$—m_am_b\cdot$
$—m_a\cdot$	M_c	$k_{13}(m_a\cdot)(M_c)$	$—m_am_c\cdot$
$—m_b\cdot$	M_a	$k_{21}(m_b\cdot)(M_a)$	$—m_bm_a\cdot$
$—m_b\cdot$	M_b	$k_{22}(m_b\cdot)(M_b)$	$—m_bm_b\cdot$
$—m_b\cdot$	M_c	$k_{33}(m_b\cdot)(M_c)$	$—m_bm_c\cdot$
$—m_c\cdot$	M_a	$k_{31}(m_c\cdot)(M_a)$	$—m_cm_a\cdot$
$—m_c\cdot$	M_b	$k_{32}(m_c\cdot)(M_b)$	$—m_cm_b\cdot$
$—m_c\cdot$	M_c	$k_{33}(m_c\cdot)(M_c)$	$—m_cm_c\cdot$

Using accepted nomenclature, the following reactivity ratios may be defined.

$$\alpha_b = \frac{k_{11}}{k_{12}} \qquad \alpha_c = \frac{k_{11}}{k_{13}}$$
$$\beta_a = \frac{k_{22}}{k_{21}} \qquad \beta_c = \frac{k_{22}}{k_{23}} \tag{14}$$
$$\gamma_a = \frac{k_{33}}{k_{31}} \qquad \gamma_b = \frac{k_{33}}{k_{32}}$$

The mole fraction of the ith monomer in the feed (f_i) is

$$f_i = \frac{M_i}{\sum M_i}$$

Substituting eq 14, 13, 12, and 11 into eq 2–7 produces eq 15–20 relating the fraction f_{ij} of various ij linkages in the copolymer in terms of the reactivity ratios and monomer feed fractions.

$$f_{aa} = P_{aa} = \frac{(f_a)^2\left[\frac{f_a}{\beta_a\gamma_a} + \frac{f_b}{\beta_a\gamma_b} + \frac{f_c}{\beta_c\gamma_a}\right]}{D} = \frac{(f_a)^2(\text{PN1})}{D} \tag{15}$$

$$f_{bb} = P_{bb} = \frac{(f_b)^2\left[\frac{f_a}{\alpha_b\gamma_a} + \frac{f_b}{\alpha_b\gamma_b} + \frac{f_c}{\alpha_c\gamma_b}\right]}{D} = \frac{(f_b)^2(\text{PN2})}{D} \tag{16}$$

$$f_{cc} = P_{cc} = \frac{(f_c)^2\left[\frac{f_a}{\alpha_c\beta_a} + \frac{f_b}{\alpha_b\beta_c} + \frac{f_c}{\alpha_c\beta_c}\right]}{D} = \frac{(f_c)^2(\text{PN3})}{D} \tag{17}$$

$$f_{bc} = P_{bc} = P_{cb} = \frac{f_bf_c}{D}\left(\frac{\text{PN2}}{\beta_c} + \frac{\text{PN3}}{\gamma_b}\right) \tag{18}$$

$$f_{ac} = P_{ac} = P_{ca} = \frac{f_af_c}{D}\left(\frac{\text{PN1}}{\alpha_c} + \frac{\text{PN3}}{\gamma_a}\right) \tag{19}$$

$$f_{ab} = P_{ab} = P_{ba} = \frac{f_af_b}{D}\left(\frac{\text{PN1}}{\alpha_b} + \frac{\text{PN2}}{\beta_a}\right) \tag{20}$$

$$D = f_a\left[f_a + \frac{f_b}{\alpha_b} + \frac{f_c}{\alpha_c}\right](\text{PN1}) + f_b\left[\frac{f_a}{\beta_a} + f_b + \frac{f_c}{\beta_c}\right](\text{PN2}) + f_c\left[\frac{f_a}{\gamma_a} + \frac{f_b}{\gamma_b} + f_c\right](\text{PN3$$

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[10] C. Walling and E. R. Briggs, *J. Amer. Chem. Soc.*, **67**, 1774 (1945).

TABLE II

ASSUMED VALUES OF COPOLYMERIZATION PARAMETERS

Monomer	e	Q
A	−0.30	0.02
B	+0.30	0.05
C	+0.60	0.20

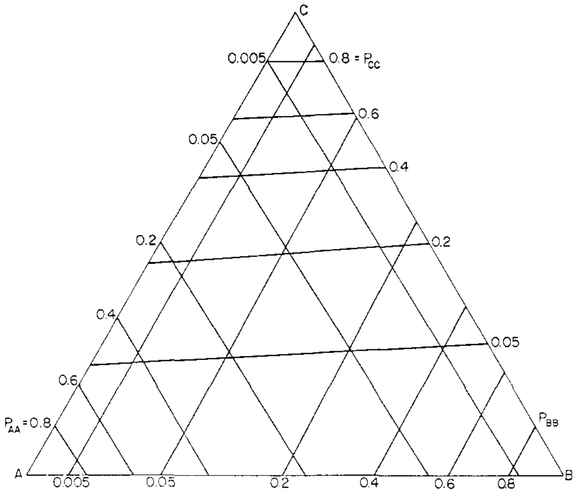

Figure 1. Calculated inter-mer linkages *vs.* polymer composition.

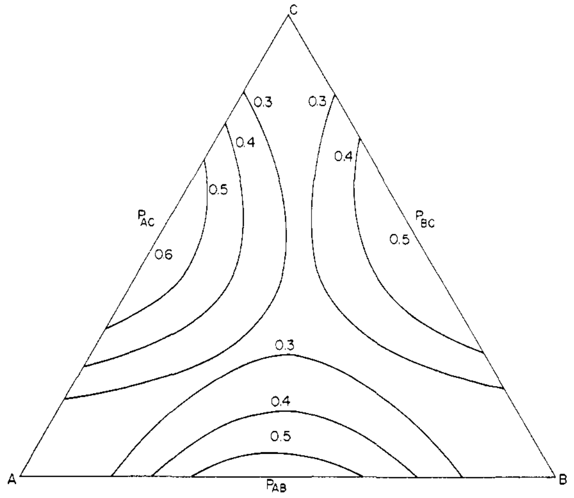

Figure 2. Calculated inter-mer linkages *vs.* polymer composition.

The various fractions of each component in the polymer (F_i) are given by eq 21–23. To illustrate the foregoing model, consider the hypothetical copolymerization of three monomers, A, B, C. Table II lists the assumed copolymerization properties of these monomers in terms of Alfrey–Price parameters Q and e. Reactivity ratios calculated by the usual equation[11] for α_b

$$F_a = \frac{f_a\left(f_a + \frac{f_b}{\alpha_b} + \frac{f_c}{\alpha_c}\right)}{D} \text{ (PN1)} \qquad (21)$$

$$F_b = \frac{f_b\left(\frac{f_a}{\beta_a} + f_b + \frac{f_c}{\beta_c}\right)}{D} \text{ (PN2)} \qquad (22)$$

$$F_c = \frac{f_c\left(\frac{f_a}{\gamma_a} + \frac{f_b}{\gamma_b} + f_c\right)}{D} \text{ (PN3)} \qquad (23)$$

$$\alpha_b = \frac{Q_b}{Q_a}\exp[-e_a(e_a - e_b)] \qquad (24)$$

are $\alpha_b = 0.33$, $\alpha_c = 0.076$, $\beta_a = 2.1$, $\beta_c = 0.27$, $\gamma_a = 5.8$, $\gamma_b = 3.3$.

A convenient way to represent the various quantities involved is by constructing contour maps. Each point in the triangular grid corresponds to a terpolymer of defined composition (the vertices are of course homopolymers, elsewhere on the axis are copolymers). Figure 1 shows contour lines for AA, BB, and CC linkages. It can be seen that these are all straight lines but are not parallel to the axes. Figure 2 shows an identical plot for AB, AC, and BC linkages. These polynomial surfaces all have their maximum value at their respective 50/50 copolymer composition, the midpoint of each axis. The maximum values are given

$$f_{ab_{max}} = \frac{1}{1 + (\alpha_b\beta_a)^{0.5}} \qquad (25)$$

by eq 25 (again shown for AB linkages). It is interesting to note that this value is a function of the product of the reactivity ratios, *i.e.*, independent of the reactivity of the monomer Q and dependent only on the polar character e of the radical adduct.

II. Variation of the Scissioning Constant $\bar{k}$

As stated previously, the over-all scission constant $\bar{k}$ is simply the weighted sum of the individual inter-mer scission constants. For given values of these constants, a stability response surface may be constructed. By varying the individual scission constants, a great variety of response surfaces are possible. Figure 3 shows the simplest type of response surface, a plane. By suitable selection of scission constants this plane can be rotated or tilted in any direction. Figure 4 shows a rising ridge displaced off center. This system also can be rotated or translated. Figure 5 shows a mound (or its mirror image a depression) with approximately elliptical contours. Not shown but also possible are saddle points (homopolymer and one ij scission constant low, other ij constants high) or simultaneous maxima and minima (one ij linkage constant high, one ij linkage constant low, homopolymer medium).

The above response surfaces were generated at a given set of reactivity ratios. Each different set of reactivity ratios will produce a different set of response surfaces. It is evident that, quite apart from mechanistic considerations, the model is versatile enough to represent adequately any stability surface likely to occur. Viewed in this light it is interesting to compare possible response surfaces with alternative six-param-

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[11] T. Alfrey and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947)

eter equations. Gorman and Hinman[12] have discussed response surfaces possible with a six-parameter quadratic polynomial subject to a constraint that $\Sigma F_i = 1.0$. In this case the quadratic simplifies to

$$\text{response} = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3$$

where β_i are adjustable constants and x_i are factor inputs subject to $\Sigma x_i = 1.0$. This surface can be a plane, ridge, or ellipse, but only one maximum or minimum (not both) is possible. Pseudo-binary systems obtained by cutting planes through this ternary surface cannot have points of inflection.

III. Estimation of Constants in Scissioning Models

The general scissioning model proposed here is of the form

$$\bar{k} = \sum f_{ij} k_{ij} \tag{26}$$

The number of constants k_{ij} to be estimated varies with the number of monomers in the system. For a polymer system containing m monomers, m homopolymer scission constants and C_2^m binary scission constants are required.

For the case $m = 1$, estimation of the homopolymer scission constant is quite straightforward. As the number of monomers increases, however, solution difficulty also increases (*e.g.*, for three monomers, six constants, for six monomers, 21 constants). Reference 9 describes a simple method of estimating inter-mer scission constants when two monomers are involved and homopolymer scission constants are known. In the general case, however, all experimental measurements are of equal uncertainty and there is no reason to place more credence in some values than in others.

In addition to the problem of estimation, there is the problem of testing the model and forming some approximate confidence intervals for quantities so estimated. Thus although a minimum of $m + C_2^m$ experimental points are required for estimation, additional points are needed for testing and forming confidence interval estimates.

Conventional estimation and testing techniques call for choosing parameter estimates $\hat{k}_{ij}$, which minimize the sum of squares of deviations about the fitted model. Although this is not the only candidate objective function, it has the following advantages: (1) when the residuals are normally distributed, with common variance, parameter estimates correspond to maximum likelihood estimates; (2) when the assumed prior distribution is relatively flat over the region of interest, the so-called locally uniform distribution, Bayesian estimates result; and (3) this objective function leads to analytically tractable equations for linear models.

Unconstrained estimation of parameters in linear equations by minimizing the residual sum of squares is a conventional technique discussed in many statistics

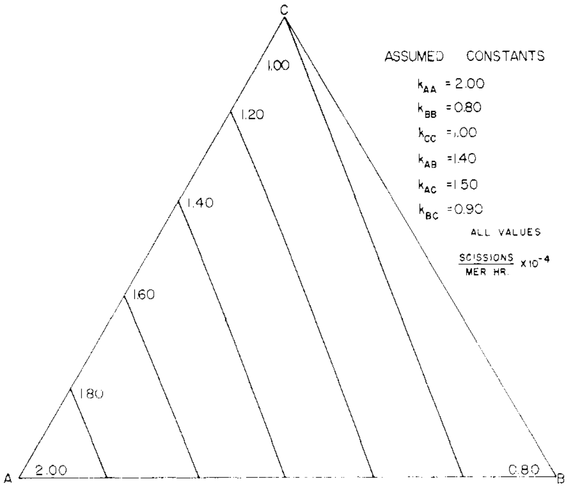

Figure 3. Over-all scission constant *vs.* polymer composition.

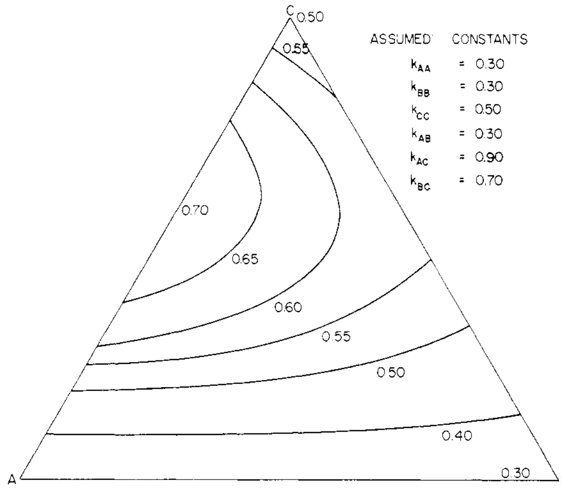

Figure 4. Over-all scission constant *vs.* polymer composition.

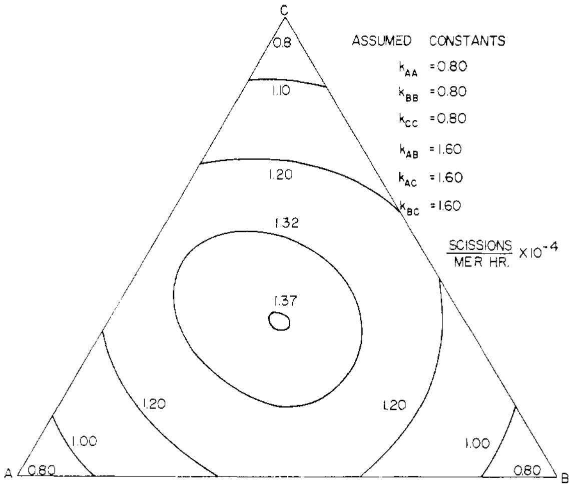

Figure 5. Over-all scission constant *vs.* polymer composition.

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[12] J. W. Gorman and J. E. Hinman, *Technometrics*, 4, 463 (1962).

Table III
ANOVA for Regression Estimation of Kinetic Constants

Source	Sum of squares	Degrees of freedom	Mean square	F. ratio	Critical values	
					α	F
Due to regression	0.684746	3	0.22825	98.81	0.05	6.59
Deviation from regression	0.009254	4	0.00230	. . .	0.01	16.69
Total	0.694000	7	. . .	. . .	0.0005	24.26

texts (see, for example, ref 13). For minimization of

$$\sum_{p=1}^{n}\left[\bar{k}_p - \sum_{j=1}^{r}\hat{k}_j f_j\right]^2$$

the estimating equations are

$$\begin{aligned} \hat{k}_1\sum_p f_1{}^2 + \ldots + \hat{k}_r\sum_p f_1 f_r &= \sum_p f_1\bar{k}_p \\ \vdots \qquad\qquad\qquad & \qquad \vdots \\ \hat{k}_1\sum_p f_r f_1 + \ldots + \hat{k}_r\sum_p f_r{}^2 &= \sum_p f_r\bar{k}_p \end{aligned} \tag{27}$$

Here the subscripts are changed for clarity ($\hat{k}_1 = k_{\mathrm{aa}}, f_1 = f_{\mathrm{aa}}$, etc., r = number of parameters, and p = observation number) or in matrix notation

$$X^{\mathrm{t}}X\hat{k} = X^{\mathrm{t}}Y \tag{28}$$

The superscript is used to denote "transpose" and

$$\hat{k} = \begin{bmatrix} \hat{k}_1 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \hat{k}_r \end{bmatrix}$$

represents the column vector of estimators. The solution becomes

$$\hat{k} = (X^{\mathrm{t}}X)^{-1}X^{\mathrm{t}}Y \tag{29}$$

Here $(X^{\mathrm{t}}X)^{-1}$ is the inverse of the matrix of normal equations. These equations correspond to the general linear hypothesis with suppression of the constant term.

An estimate S^2 of σ^2 is given by (using matrix notation)

$$S^2 = \frac{1}{n - r}(Y^{\mathrm{t}}Y - \hat{k}^{\mathrm{t}}X^{\mathrm{t}}Y) \tag{30}$$

where n = the number of points.

A $1 - \alpha$ confidence interval for any of the constants $\hat{k}_i$ estimated is given by

$$\hat{k}_j - t_{n-r(\alpha/2)}S\sqrt{c_{jj}} < \kappa < \hat{k}_j + t_{n-r(\alpha/2)}S\sqrt{c_{jj}} \tag{31}$$

where κ represents the true value of k_j, c_{jj} is the jth diagonal term of the inverse matrix $(X^{\mathrm{t}}X)^{-1}$, and $t_{n-r(\alpha/2)}$ is the value of Student's t for $n - r$ degrees of freedom. Simultaneous $1 - \alpha$ confidence intervals for all k's can also be generated (see, for example, Scheffe[14]).

As an example of these techniques the data from ref 9 for the two-monomer case is analyzed. The initial analysis regarded the homopolymer scission constants as fixed and estimated the copolymer constant k_{ab}. However, estimates of homopolymer scission constants are of comparable uncertainty, suggesting that these parameters should appear in estimation equations. The system investigated was a vinyl acetate (a), ethyl acrylate (b) copolymer. Estimates of scission constants were $k_{\mathrm{aa}} = 0.79$, $k_{\mathrm{bb}} = 1.6$, $k_{\mathrm{ab}} = 1.6$ (all values: $\times 10^{-4}$ scission/mer hr). The normal equations are

$$\begin{aligned} \sum f_{\mathrm{aa}}\bar{k}_p &= (\sum f_{\mathrm{aa}}{}^2)k_{\mathrm{aa}} + (\sum f_{\mathrm{aa}}f_{\mathrm{bb}})k_{\mathrm{bb}} + (\sum f_{\mathrm{ab}}f_{\mathrm{aa}})k_{\mathrm{ab}} \\ \sum f_{\mathrm{bb}}\bar{k}_p &= (\sum f_{\mathrm{aa}}f_{\mathrm{bb}})k_{\mathrm{aa}} + (\sum f_{\mathrm{bb}}{}^2)k_{\mathrm{bb}} + (\sum f_{\mathrm{ab}}f_{\mathrm{bb}})k_{\mathrm{ab}} \\ \sum f_{\mathrm{ab}}\bar{k}_p &= (\sum f_{\mathrm{aa}}f_{\mathrm{ab}})k_{\mathrm{aa}} + (\sum f_{\mathrm{bb}}f_{\mathrm{ab}})k_{\mathrm{bb}} + (\sum f_{\mathrm{ab}}{}^2)k_{\mathrm{ab}} \end{aligned}$$

Solution of these equations through the inverse yields estimates $k_{\mathrm{aa}} = 0.78$, $k_{\mathrm{bb}} = 1.62$, $k_{\mathrm{ab}} = 1.61 \times 10^{-4}$ scission/mer hr. From eq 30, $S = 0.0481$, from eq 27, $c_{11} = 0.7326$, $c_{22} = 0.6267$, $c_{33} = 1.3572$, which yields the following confidence intervals for the k's: $k_{\mathrm{aa}} = 0.782 \pm 0.114$, $k_{\mathrm{bb}} = 1.624 \pm 0.106$, $k_{\mathrm{ab}} = 1.606 \pm 0.156$. Table III shows the ANOVA for this analysis.

The error mean square is not significantly higher than that of replicate measurements. Figure 6 shows a plot of gauss^{-1} $i/(n + 1)$ *vs.* ordered residual, which suggests the errors are normally distributed. No significant correlations were observed in plots of residuals *vs.* k_{obsd}, $k_{\mathrm{predicted}}$, f_{ij}'s, or run number. The use of such plots may be called to question due to the correlation which exists among the residuals. However, as a practical matter, the effect of correlation upon graphical procedures is negligible except when the ratio $(n - r)/n$ is quite small.[15] From the above it follows that the model successfully "postdicts" the experimental data.

Another approach to the estimation problem is to regard the reactivity ratios as variables rather than constants and estimate these simultaneously. In principle this is easily done; however, the problem becomes highly nonlinear and numerical search techniques might have to be used. In addition, the number of variables becomes quite substantial even for copolymers containing only three or four monomers. Nine constants need be estimated for a terpolymer, for example. In addition, it turns out that the actual fraction of inter-mer linkages is only a weak function of the reactivity ratios, suggesting that likelihood regions would tend to be flat in the reactivity ratio parameter space (*cf.*, the one-half-power damping factor in eq 25).

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(13) F. A. Graybill, "An Introduction to Linear Statistical Models," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1961.

(14) H. Scheffe, "The Analysis of Variance," John Wiley and Sons, Inc., New York, N. Y., 1959.

(15) N. R. Draper and H. Smith, "Applied Regression Analysis," John Wiley and Sons, Inc., New York, N. Y., 1967, p 94.

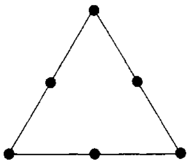
IV. Experimental Design

Having discussed the model, estimation of model parameters, and tests of fit for the model, it is natural to consider the topic of experimental design.

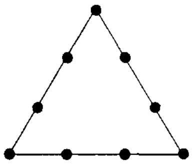
One design problem is immediately apparent—the constraints on and correlation among the f_{ij}'s makes an orthogonal design impossible. Thus, the conventional designs (factorial, fractional factorial, etc.) are unsuitable for this case. (Since all estimates of the kinetic constants are correlated, strictly speaking a joint likelihood surface should be used to indicate confidence in the parameters rather than individual confidence statements.)

A second complication is that the experimenter generally chooses experimental designs in terms of the copolymer (F_i) or comonomer composition (f_i). Random errors in feed or polymer composition lead to bias in linkage fractions (f_{ij}) owing to the nonlinear nature of the transformation.

One approach to experimental design for this problem is to select certain specific designs developed especially for mixtures and examine the variance contours of these designs for this model. Scheffe[16] and later Gorman and Hinman[12] have developed designs of this type. The factor space (F_a, F_b, F_c) for experiments is a simplex and the designs have come to be called simplex lattice designs. These designs give a uniformly spaced distribution of points over the factor space. The proportions used for each factor have $m + 1$ equally spaced values from 0 to 1, $F_i = 0, 1/m, 2/m\ldots, 1$, and all possible mixtures with these proportions are used. Typical designs for three-component systems are



a



b

The utility of any of these designs can be assessed by examining the variance of the response at any point. The variance of a predicted response $\bar{k}$ at factor levels $(f_1\ldots f_r)$ is given by[17]

$$\text{var}\ \bar{k} = S^2[x^t(X^tX)^{-1}x] \qquad (32)$$

where $x = r \times 1$ vector in which the ith element is f_i and $(X^tX)^{-1}$ = inverse of the matrix of normal equations. The term in brackets on the right-hand side acts to multiply the sample variance by a factor which depends on the point in question $(f_1\ldots f_r)$ and the basic design (c_{ij}'s). Variance contours can be normalized by dividing the variance at any point by the estimate (S^2) of the sample variance which of course is simply the bracketed term referred to above. The variation of this term with composition (F_i) for a given design yields a map showing the relative reliability of predicted responses (mean scission constant).

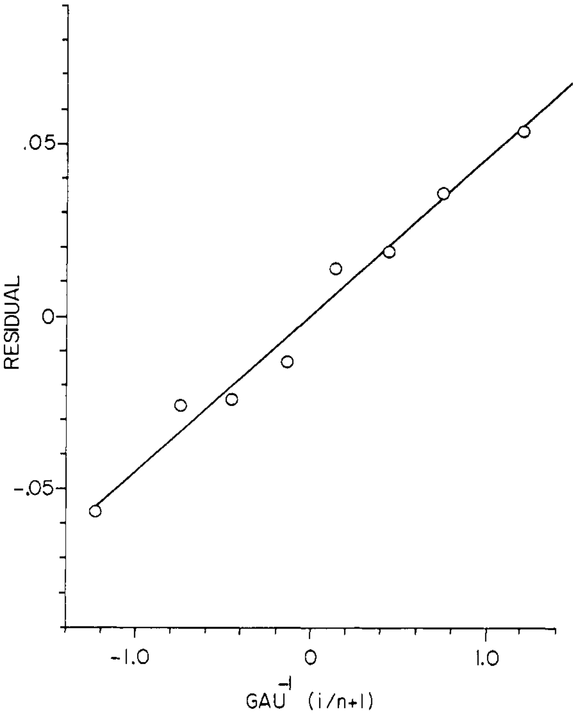


Figure 6. Examination of residuals from fitted model.

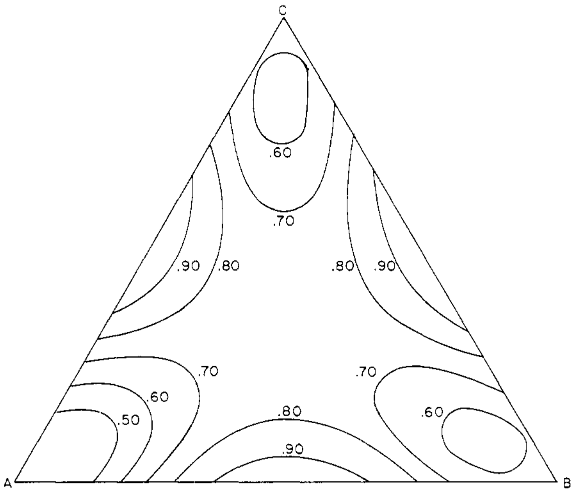


Figure 7. Variance contours for design a1 *vs.* polymer composition.

Figures 7, 8, and 9 show variance contours constructed for designs a with replicates of corner points, a with replicates of middle points, and b, respectively. In each case the number of experimental points required is the same (nine). These variance contours were constructed taking assumed values of the reactivity ratios to transform the design matrix, given in terms of F_i, to the actual design matrix (f_{ij}'s). The normal equation matrix (obtained from the f_{ij} design matrix) is then inverted to yield the elements c_{ij} necessary to calculate var $\bar{k}$. A computer program has been written to

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(16) H. Scheffe, *J. Roy. Stat. Soc.*, **B20**, 344 (1958).

(17) F. A. Graybill, see ref 13, p 122.

Table IV
Confidence Interval (C.I.) Multipliers for Simplex Designs

Constant estd	Design a1	Design a2	Design b
	Multiplier		
k_{aa}	0.71	1.00	0.95
k_{bb}	0.71	1.00	0.95
k_{cc}	0.71	1.00	0.95
k_{ab}	1.88	1.42	1.65
k_{ac}	1.70	1.27	1.50
k_{bc}	2.00	1.53	1.76
Mean	1.28	1.20	1.29
Std dev	0.64	0.24	0.38

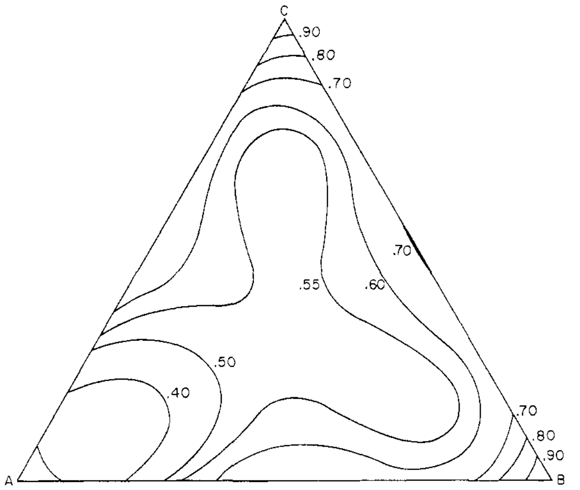

Figure 8. Variance contrours for design a2 *vs.* polymer composition.

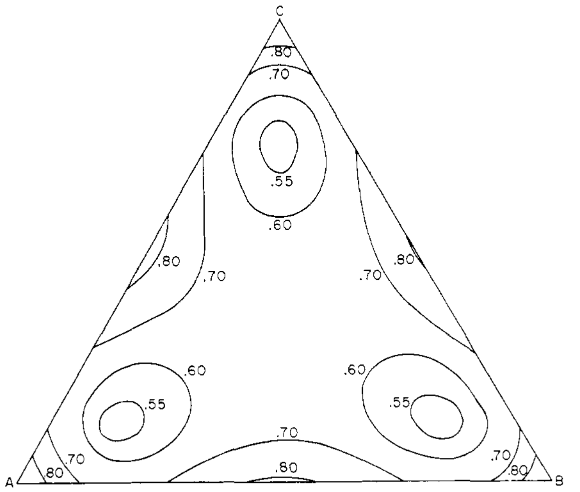

Figure 9. Variance contours for design b *vs.* polymer composition.

generate these contours from design and reactivity data and is available on request.

Although variance contours given in Figures 7–9 were calculated for a specific set of reactivity ratios, certain general features are evident.

(1) Variance contours for symmetrical F designs will, in general, be asymmetrical; thus if symmetrical variance contours are desired some iterative process must be employed to generate asymmetrical F designs. The degree of dissymmetry for the reactivity ratios used in this example is probably not severe enough to warrant the effort.

(2) Comparison of design a1 with a2 (replication of middle points *vs.* replication of corner points) indicates the general superiority of middle point replication. This concurs with intuitive notions.

(3) Design b yields variance contours which are intermediate between a1 and a2.

Another way of illustrating the comparison between these designs is to examine confidence intervals for estimation of scission constants. The width of the confidence interval is (from eq 31) proportional to $(c_{ii})^{0.5}$. Table IV shows $(c_{ii})^{0.5}$ values for each constant estimated in each of the designs.

There are basically two criteria that might be used in evaluating designs: (a) select a design that has the minimum average C.I. width or (b) since in general all constants are of equal importance a design might be selected which minimizes the variability of individual C.I. widths. It can be seen that design a2 is best by either criterion. Again design b dominates design a1.

Design b, however, is suitable for tests of linearity of the model as well as efficient estimations of responses or individual scission constants. Since the experimenter is at least as concerned with testing the model as with prediction of responses (certainly in the initial phases of the investigation), design b appears the most useful.

Critique of the Model. Most of the criticism of the model itself can be traced to simplification at various points in the derivation. In all cases it is possible to overcome these criticisms at the expense of simplicity or analytical tractability.

Specific points at which this occurs are basically twofold: (A) in the original description of type of links considered and (B) in the derivation of equations necessary for calculating fractions of these links. The following paragraphs discuss these points and suggest modification and extension.

A. 1. The Problem of Anomalous Links. Specifically ignored in consideration of linkage types in a copolymer were two "common" types of anomalous links—head-to-head links and branches. While little data are available to judge the stability of head-to-head links, it is generally accepted that substantially branched materials are less stable than corresponding linear materials. Branching occurs in most polymers to an extent determined by monomer type, catalyst, temperature, time, impurities, etc. In a copolymer, the variables are similar with the added factor of comonomer type and concentration. One approach to the model would be to view the observed scission constant of the homopolymer as being an effective scission constant composed of whatever anomalous links are present in the homopolymer. If the fraction of these anomalous links is not a function of sequence length (of homopolymer mer) or of comonomer type in a copolymer, then the model is still quite valid. We realize, however, that inter-mer scission constants are functions of the polymerization variables. If the above is not true (or approximately true) then a homopolymer might be viewed as a "copolymer" of regular and anomalous links. Since for a terpolymer there are nine distinct branching possibilities (A, B, or C branching from A, B, or C), as many as nine additional kinetic constants would be required to specify the system, not considering whatever constants are necessary to describe the branching mechanism.

2. Nearest Neighbor Effects. In the model, the stability of any link was assumed to be independent of the presence and type of neighboring links. If, however, the effect of a given linkage extends beyond this linkage, then additional constants are necessary. For a terpolymer, in the case of an A–A linkage, for example, the following scission constants need to be included: k_{aaaa}, k_{aaab}, k_{aaac}, k_{baab}, k_{baac}, k_{caac}. A total of 36 constants would be required for complete description of the system.

B. Two major simplifications were made in the derivation of eq 15–20. The first was that the effect of penultimate and ante-penultimate units was negligible, the second assumed constant feed ratios of monomers (f_i). If the first assumption is invalid, alternate treatments are available.[18] If the second is invalid (as, for example, in a batch or semibatch process), then eq 15–20 may be integrated numerically to give appropriate values of f_{ii}.

(18) E. Merz, T. Alfrey, and G. Goldfinger, *J. Polymer Sci.*, **1**, 75 (1946).

Line Width of Nuclear Magnetic Resonance High Resolution Spectra of Vinyl Polymers

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Received November 21, 1967

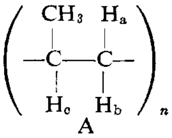
ABSTRACT: The line widths of high resolution nmr spectra of vinyl polymers were studied with particular reference to isotactic polypropylene. It was observed, by deuterium decoupling experiments, that for polypropylene it is the coupling constants through several bonds that mainly determine the broadening of the lines. By eliminating them, we obtained spectra with resonance line widths of the same order of magnitude as observed on small organic molecules.

Let us consider a nondeuterated vinyl polymer in solution. The nmr spectrum of this solution generally does not exhibit well-resolved lines. In the presence of suitable solvents, the widths of the resonance lines can be decreased by increasing the temperature and decreasing the concentration. However, even in the best circumstances, at high temperature, the width of the resonance lines of a polymer ranges from a minimum of 1 to several cycles per second. The purpose of this research is to establish why the bands undergo this residual broadening.

A resonance signal may be broadened as a result of several reasons: I, insufficient average of magnetic dipole–dipole interactions in the solutions, due to relatively slow motion of the chains;[1] II, excessive viscosity of the solutions;[1] III, spectra that are not completely of the first order, with consequent broadening of the experimental bands, which are actually multiple;[2] IV, small long-range coupling constants; and V, not sufficiently rapid exchange among the various conformers so that the same proton may be situated in magnetically nonequivalent surroundings.

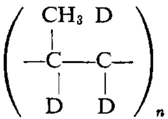
It was shown that the line width of a polymer in solution is independent of the molecular weight of the polymer,[1–3] so the viscosity of the solution will not be considered here. Nevertheless, we operated under experimental conditions such that the solution might flow on the test tube walls. If a polymer is not sterically pure, its spectrum consists of the superimposition of the spectra of various components,[4] owing to the presence of different types of tetrads and pentads that may give partly superimposed bands; thus an artificial broadening of the lines is created, due only to the poor resolution of spectrometers. To exclude this difficulty, we mainly used isotactic polypropylene because this polymer can be obtained sterically pure.[5,6]

Isotactic Polypropylene. Products A–E have been studied. All isotactic polymers considered were high



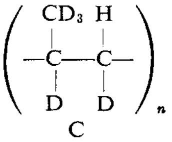
$$\left(\begin{array}{c} \mathrm{CH_3}\quad \mathrm{H_a} \\ |\qquad | \\ -\mathrm{C}-\mathrm{C}- \\ |\qquad | \\ \mathrm{H_c}\quad \mathrm{H_b} \end{array}\right)_n$$

A



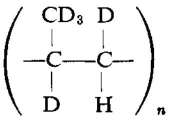
$$\left(\begin{array}{c} \mathrm{CH_3}\quad \mathrm{D} \\ |\qquad | \\ -\mathrm{C}-\mathrm{C}- \\ |\qquad | \\ \mathrm{D}\quad \mathrm{D} \end{array}\right)_n$$

B



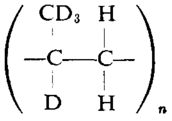
$$\left(\begin{array}{c} \mathrm{CD_3}\quad \mathrm{H} \\ |\qquad | \\ -\mathrm{C}-\mathrm{C}- \\ |\qquad | \\ \mathrm{D}\quad \mathrm{D} \end{array}\right)_n$$

C



$$\left(\begin{array}{c} \mathrm{CD_3}\quad \mathrm{D} \\ |\qquad | \\ -\mathrm{C}-\mathrm{C}- \\ |\qquad | \\ \mathrm{D}\quad \mathrm{H} \end{array}\right)_n$$

D



$$\left(\begin{array}{c} \mathrm{CD_3}\quad \mathrm{H} \\ |\qquad | \\ -\mathrm{C}-\mathrm{C}- \\ |\qquad | \\ \mathrm{D}\quad \mathrm{H} \end{array}\right)_n$$

E

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(2) P. L. Corio, *Chem. Rev.*, **60**, 363 (1960).

(3) A. Odajima, *J. Phys. Soc. Japan*, **14**, 777 (1959).

(4) F. A. Bovey, E. W. Anderson, D. C. Douglass, and J. A. Manson, *J. Chem. Phys.*, **39**, 1199 (1963).

(5) A. Zambelli, A. L. Segre, M. Farina, and G. Natta, *Makromol. Chem.*, in press.

(6) A. Zambelli, private communication.