Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Jenkins, Aubrey D.(2000) 'THE REVISED PATTERNS OF REACTIVITY SCHEME. PART 6. A GENERAL FORMULATION OF THE SCHEME AND THE "ALTERNATING TENDENCY"', Journal of Macromolecular Science, Part A, 37: 12, 1547 — 1569

To link to this Article: DOI: 10.1081/MA-100102325

URL: http://dx.doi.org/10.1081/MA-100102325

J.M.S.—PURE APPL. CHEM., A37(12), pp. 1547–1569 (2000)

THE REVISED PATTERNS OF REACTIVITY SCHEME. PART 6. A GENERAL FORMULATION OF THE SCHEME AND THE "ALTERNATING TENDENCY"

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ABSTRACT

For the last 50 years, the prediction of monomer reactivity ratios has been based on the Alfrey-Price *Q*-*e* Scheme, despite its theoretical weaknesses and its relatively low level of accuracy. The Patterns of Reactivity Scheme, in its revised form, is much more accurate and applies to transfer reactions, as well as to copolymerization. It is now shown that it can be formulated more generally than previously and, with respect to the Alternating Tendency, it is found to provide a good correlation with experimental results.

INTRODUCTION

One of the most important aspects of the study of copolymerization is the relationship between the composition of the monomer feed (i.e., the relative monomer concentrations, best expressed as the molar ratio) and that of the resulting copolymer. For binary copolymerization with monomers M_1 and M_2, this is usually written in the form known as the copolymer composition equation, copolymerization equation or copolymer equation:

$$R_p = R_m(\boldsymbol{r}_{12}R_m + 1)/(\boldsymbol{r}_{21} + R_m)$$

where R_m is equal to $[M_1]/[M_2]$ in the monomer mixture, and R_p is equal to $[M_1]/[M_2]$ in the polymer formed. Apart from the monomer composition ratio, this expression contains two quantities, the *monomer reactivity ratios* $\boldsymbol{r}_{12}$ and $\boldsymbol{r}_{21}$, characteristic of the particular monomer pair. Obviously, it would be extremely useful to be able to predict the values of $\boldsymbol{r}_{12}$ and $\boldsymbol{r}_{21}$ and hence the composition of any copolymer produced from any pair of monomers at any concentration ratio. Virtually the only way that has been employed to achieve this objective is based on the Alfrey-Price *Q-e* formulation [1] of the equation for a velocity constant for the addition of a (polymer) radical (species 1) to a monomer (species 2), This is as follows where the subscripts 1 and 2 denote the two participating species.

$$\boldsymbol{k}_{12} = \boldsymbol{Q}_1\boldsymbol{Q}_2\exp(- \boldsymbol{e}_1\boldsymbol{e}_2)$$

or

$$\log \boldsymbol{k}_{12} = \log \boldsymbol{Q}_1 + \log \boldsymbol{Q}_2 - 0.4343\boldsymbol{e}_1\boldsymbol{e}_2 \qquad (1)$$

where $\boldsymbol{Q}_1$ represents the intrinsic reactivity of the polymer radical derived from monomer **1**,

$\boldsymbol{Q}_2$ represents the intrinsic reactivity of monomer **2**,

$\boldsymbol{e}_1$ represents the polarity of the polymer radical derived from monomer **1**, and

$\boldsymbol{e}_2$ represents the polarity of the monomer **2**.

Recently, the Revised Patterns of Reactivity Scheme [2-5] has been developed, retaining much of the general format of the *Q-e* Scheme but with the following parameters replacing those selected by Alfrey and Price.

$\boldsymbol{k}_{1S}$ represents the intrinsic reactivity of the polymer radical derived from monomer **1**,

$\boldsymbol{v}_2$ represents the intrinsic reactivity of monomer **2**,

$\boldsymbol{\sigma}_1$ (see below) represents the polarity of the polymer radical derived from monomer **1**, and $\boldsymbol{u}_2$ represents the polarity of the monomer **2**.

Here, and in other symbols, the subscript "**S**" denotes styrene, and the Hammett sigma constant $(\boldsymbol{\sigma}_p)$ for a substituent in the para position on a benzene ring can be used to represent the influence on the polarity of the radical of the substituent(s) on the carbon atom bearing the unpaired electron; for the radical derived from monomer 1, this is symbolized as σ_1, and so on. This is how the theory was developed at the beginning of Part 2 [2] of this series of papers. In the present paper, we also consider a more general formulation of the scheme in which the standard of intrinsic radical reactivity is not $\boldsymbol{k}_{1S}$ but some other (unspecified) criterion; it is seen that this leads to a substantial loss of some of the more useful aspects of the procedure. The successful application of the scheme to the study of the alternating tendency is also presented, and a further test of the scheme is examined.

The Basis of the Revised Patterns Scheme

In the Revised Patterns Scheme, the parallel to Equation 1 is Equation 2.

$$\log \boldsymbol{k}_{12} = \log \boldsymbol{k}_{1S} + \boldsymbol{u}_2\boldsymbol{\sigma}_1 + \boldsymbol{v}_2 \qquad (2)$$

The term log $\boldsymbol{k}_{11}$ is now subtracted from both sides to give Equation 3

$$\log \boldsymbol{r}_{12} = \log \boldsymbol{r}_{1S} - \boldsymbol{u}_2\boldsymbol{\sigma}_1 - \boldsymbol{v}_2 \qquad (3)$$

Equation 3 is essentially a postulate, based on the same principle as the *Q-e* scheme, but it is the only feature that is assumed in the Revised Patterns treatment, and it has previously been shown that the predictions made on this basis are much closer to the experimental values than are those of the *Q-e* Scheme [3].

A test of the validity of Equation 3 is to plot the LHS of the rearranged form Equation 4, below, against $\boldsymbol{\sigma}_1$ for a series of monomers **1** but with a chosen monomer **2**.

(All the monomer reactivity ratio data employed in our work are taken from Greenley's compilations [6, 7]).

$$\log \boldsymbol{r}_{12} - \log \boldsymbol{r}_{1S} = -\boldsymbol{u}_2\boldsymbol{\sigma}_1 - \boldsymbol{v}_2 \qquad (4)$$

This test was performed in Figure 1 of Part 2 [2], with acrylonitrile as monomer **2** and denoted by subscript "**A**", the monomers **1** being the members of the Basic Monomer Set [2], that is styrene, methyl methacrylate, methyl acrylate, methacrylonitrile and acrylonitrile, i.e.,

$$\log \boldsymbol{r}_{\mathbf{1A}} - \log \boldsymbol{r}_{\mathbf{1S}} = -\boldsymbol{u}_{\mathbf{A}}\boldsymbol{\sigma}_{\mathbf{1}} - \boldsymbol{v}_{\mathbf{A}} \tag{5}$$

From the slope of this plot, $\boldsymbol{u}_{\mathbf{A}} = -2.60$ and, from the intercept on the ordinate axis at $\boldsymbol{\sigma}_{\mathbf{1}} = 0$, $\boldsymbol{v}_{\mathbf{A}} = 0.42$.

If Equation 5 is reduced to the particular case where monomer **1** is styrene (subscript S), we find that

$$\log \boldsymbol{r}_{\mathbf{SA}} - \log \boldsymbol{r}_{\mathbf{SS}} = -\boldsymbol{u}_{\mathbf{A}}\boldsymbol{\sigma}_{\mathbf{S}} - \boldsymbol{v}_{\mathbf{A}}$$

Now, log $\boldsymbol{r}_{\mathbf{SS}}$ is necessarily identical to zero and $\boldsymbol{\sigma}_{\mathbf{S}}$ is very close to zero. [Although the value of $\boldsymbol{\sigma}_{\mathbf{p}}$ for the phenyl group is not included in the IUAPC approved list compiled by Shorter [8, 9], it was determined by Hammett, on the basis of data provided by Kindler [10], to be +0.009. Berliner and Liu [11] comment that the use of an alternative value for the pK_a for benzoic acid would instead have produced the figure -0.008; in these circumstances, the assumption that it can be taken to be effectively zero would appear to be reasonable.] Taking $\boldsymbol{\sigma}_{\mathbf{S}} = 0$ involves a very small approximation, if any, so that log $\boldsymbol{r}_{\mathbf{SA}}$ must be virtually equal to $-\boldsymbol{v}_{\mathbf{A}}$; from Greenley's listing [6] , $\boldsymbol{r}_{\mathbf{SA}} = 0.38$, hence log $\boldsymbol{r}_{\mathbf{SA}} = -\boldsymbol{v}_{\mathbf{A}} = -0.42$, in complete agreement with the value deduced above.

If the case is now considered where monomer **2** is acrylonitrile while monomer **1** is some selected monomer, say **X**, an rearrangement of Equation 4 produces a general expression for $\boldsymbol{\sigma}_{\mathbf{X}}$, exclusively in terms of polymerization data.

$$\boldsymbol{\sigma}_{\mathbf{X}} = -(1/\boldsymbol{u}_{\mathbf{A}})[\log \boldsymbol{r}_{\mathbf{XA}} - \log \boldsymbol{r}_{\mathbf{XS}} + \boldsymbol{v}_{\mathbf{A}}] \tag{6}$$

Since the values of $\boldsymbol{u}_{\mathbf{A}}$ and $\boldsymbol{v}_{\mathbf{A}}$ are known (see above), this equation can be condensed to:

$$\boldsymbol{\sigma}_{\mathbf{X}} = 0.385\log[\boldsymbol{r}_{\mathbf{XA}}/0.377\boldsymbol{r}_{\mathbf{XS}}] \tag{7}$$

It thus appears that, for any monomer, one can calculate $\boldsymbol{\sigma}_{\mathbf{X}}$ provided that the monomer reactivity ratios for the separate copolymerizations of monomer **x** with (i) acrylonitrile and (ii) styrene are known. It is indeed tempting to suggest that this provides a method for the evaluation of σ for groups for which it has not been determined by other means.

From this point on, there is a choice: either one can continue to use the experimental σ_p parameters, derived from the ionization of substituted benzoic acids and tabulated by Shorter on behalf of IUPAC [8, 9], or one can rely exclusively on polymerisation data and employ Equation 7. If the latter course is adopted, the symbol π is used rather than σ for the result in order to emphasise the difference in procedure, and the basic Equation 3 is rewritten as 3a, thus:

$$\log r_{12} = \log r_{1S} - u_2\pi_1 - v_2 \tag{3a}$$

In fact, where comparison is possible, σ_x and π_x are found to have virtually identical values (See Figure 2 of Part 2 [2]).

The u and v parameters for any monomer of interest, **X**, can be derived by a graphical procedure exactly parallel to that employed above for acrylonitrile. The particular monomer is treated as monomer **2** in Equation 4and the same series of monomers as listed previously (the Basic Monomer Set) is preferably used as the series of monomers **1**, plotting the function [$\log r_{1X} - \log r_{1S}$] *versus* either σ_1 or π_1. The slope and the intercept give u_X and v_X unambiguously, and no arbitrary assignment of values is required for any of the reactivity parameters. The relevant plots for the members of Basic Monomer Set were presented in Figure 3 of Part 2 [2].

The use of σ is attractive in that it links this aspect of polymerization chemistry to physical chemistry in general, but the drawback is that rather few values of σ have been evaluated for groups found in vinyl monomers. The alternative of using π affords a measure of satisfaction in that all the data employed come from studies of polymerisation reactions. In practice, the only thing that matters is that the value used is sound.

An Alternative Formulation of the Basic Equation

A variant on this method of calculation is provided by consideration of Equation 2 together with the corresponding relation for the (trivial) case that monomer **2** is identical to monomer **1,** thus:

$$\log k_{11} = \log k_{1S} + u_1\pi_1 + v_1 = 0 \tag{8}$$

and, hence

$$\log r_{12} = u_1\pi_1 + v_1 - u_2\pi_1 - v_2 \tag{9}$$

or $$\log r_{12} = \pi_1(u_1 - u_2) + (v_1 - v_2) \tag{10}$$

Equation 10 provides a way of calculating r_{12} without explicitly involving log r_{1S} so, Equations 3a and 10 offer alternative routes to the desired solution. The former only requires a knowledge of four quantities but the latter involves five; as there is inevitably a degree of uncertainty in each of the experimental parameters, the former might be expected to give the more accurate results. For the twenty monomer reactivity ratios that relate to all binary combinations in the Basic Monomer Set (listed above), the percentage discrepancy, ***pd***, between the values calculated from Equation 10 and those obtained experimentally is 17.6 [As defined previously [3], ***pd*** $= 100(r_{\text{calculated}} - r_{\text{experimental}})/r_{\text{calculated}}$]; on the basis of Equation 3a, the corresponding ***pd*** is 7.5, as was reported [3]. In line with expectations, the latter result is more accurate than that obtained from the application of Equation 10.

Summary of the U, V Scheme

The foregoing material describes that part of the procedure that is called the **U, V Scheme**. To summarize, if it is desired to calculate the monomer reactivity ratios for the copolymerization of monomers **1** and **2**, it is only necessary to look up r_{1A}, r_{1S}, r_{2A}, r_{2S} in Greenley's lists [6, 7], and then calculate π_1 and π_2 as explained above. The values of u_1, v_1, u_2, v_2 are deduced from plots of [log r_{X1} - log r_{XS}] and [log r_{X2} - log r_{XS}] *v*s. either σ_X or π_X, the monomers **X** being styrene, methyl methacrylate, methyl acrylate, methacrylonitrile and acrylonitrile. Substitution, as appropriate, in the equations:

$$\log r_{12} = \log r_{1S} - u_2\pi_1 - v_2 \tag{11}$$

$$\log r_{21} = \log r_{2S} - u_1\pi_2 - v_1 \tag{12}$$

gives the required results. (A full example of this procedure, called the **U,V Scheme**, is provided in Part 3 for 2-chlorobutadiene and 2-vinyl pyridine [3].)

The A, S Scheme

A condensed version of the procedure, called the **A, S Scheme**, is available for circumstances in which only the monomer reactivity ratios for the copolymerization of monomers **1** and **2** with styrene and acrylonitrile are to be employed; it is then possible to bypass the calculation of ***u*** and ***v*** values, and simply substitute the appropriate values of monomer reactivity ratios in the right-hand side of Equation 13 to obtain r_{12}.

$$\log(r_{12}) = \frac{\log[(r_{1S})(r_{S2}]) - [\log(r_{AS})(r_{S2})/(r_{A2})][\log(\mathbf{r}_{SA})(r_{1S})/(r_{1A})]}{\log[(r_{AS})(\mathbf{r}_{SA})]} \qquad (13)$$

A General Formulation

As presented above, the scheme contains the assumption that the intrinsic reactivity of a radical is measured by the value of k_{1S} and its polarity by σ_1 (or π_1); it then follows that log $r_{S2} = -v_2$ and $\sigma_S = \pi_S = u_S = v_S = 0$. Although the electronic influence of the phenyl group in the styryl radical is unlikely to be large, it may seem to be an over-simplification to assume it to be zero. It is therefore of interest to explore the consequences of abandoning the use of k_{1S} as the criterion of intrinsic radical reactivity and replacing it by an alternative quantity, say ρ_1. Using π_1 to represent radical polarity, the basic Equation 2 for a velocity constant thus becomes

$$\log k_{12} = \rho_1 + u_2\pi_1 + v_2 \qquad (14)$$

Combining Equation 14 with the special cases that (i) monomer 2 is identical to monomer 1 and (ii) monomer 2 is S, i.e.,

$$\log k_{11} = \rho_1 + u_1\pi_1 + v_1 \qquad (15)$$

and

$$\log k_{1S} = \rho_1 + u_S\pi_1 + v_S \qquad (16)$$

We have

$$\log r_{12} = \log r_{1S} - \pi_1(u_2 - u_S) - (v_2 - v_S) \qquad (17)$$

or $\log r_{12} = \pi_1(u_1 - u_2) + (v_1 - v_2)$

The last equation has already appeared as Equation 10 above, so the adoption of the undefined parameter (ρ_1) of radical polarity has had no effect on this result but Equation 17 shows that it is now necessary to replace u_2 and v_2 by ($u_1 - u_S$) and ($v_2 - v_S$), respectively. It is no longer valid to write log $r_{S2} = -v_2$ or u_S

$= v_S = 0$; neither can Equation 13 be employed, which is disturbing in view of the success [3] of this extremely convenient procedure. It is, of course, not possible to evaluate u_S and v_S absolutely but values could be assumed, if evidence for them were available, and the u_S and v_S values, as reported previously, would have to be adjusted accordingly. The impossibility of evaluating u_S and v_S is parallel to the problem encountered in the *Q-e* Scheme which obliged its authors to assume arbitrary (controversial) values for Q_S and e_S.

An additional cause for concern is that Equation 6 would no longer be valid because there would be no basis for assuming that $\rho_S = 0$, and σ_1 would become a function of ρ_S. The very satisfactory experimental correlation of σ_1 and π_1, demonstrated previously [2], strongly suggests that it is unnecessary to employ this general formulation in practice, but it has to be recognised that it is, in principle, more fundamental.

A Further Test of the U, V Scheme

An interesting test of the scheme arises from a consideration of the calculation of the trivial monomer reactivity ratio r_{11}, which is necessarily identical to unity ($=k_{11}/k_{11}$). In Part IV, it was shown [4] that the scheme provides a good estimate of r_{11} values when tested for over 100 monomers. But a further test can be devised by writing the equation for log r_{11} in the following manner, remembering that log r_{S1} is equal to $-v_1$ (see above).

$$\log r_{11} = \log r_{1S} - u_1\pi_1 + \log r_{S1} = 0 \tag{18}$$

$$\text{or} \quad \log(r_{1S}r_{S1}) = \log r_{1S} + \log r_{S1} = u_1\pi_1 \tag{19}$$

A plot of the left hand side of Equation 19 vs. its right hand side is presented in Figure 1 for a total of 90 monomers, and the line of unit slope drawn thereupon corresponds to perfect agreement; the data are listed in Table 1. While a measure of experimental error is inevitably apparent, the general trend of agreement is clear. The monomers for which data were employed are the vinyl monomers listed in the Table of Patterns of Reactivity Parameters in the 4th edition of the Polymer Handbook [12] for which the necessary data are available; 1,2 disubstituted monomers have been excluded on account of their different structural features.

The result that the sum of the logarithms of the two complementary monomer reactivity ratios for the copolymerization of styrene with any selected monomer is given by the simple product of the polarity parameters for that

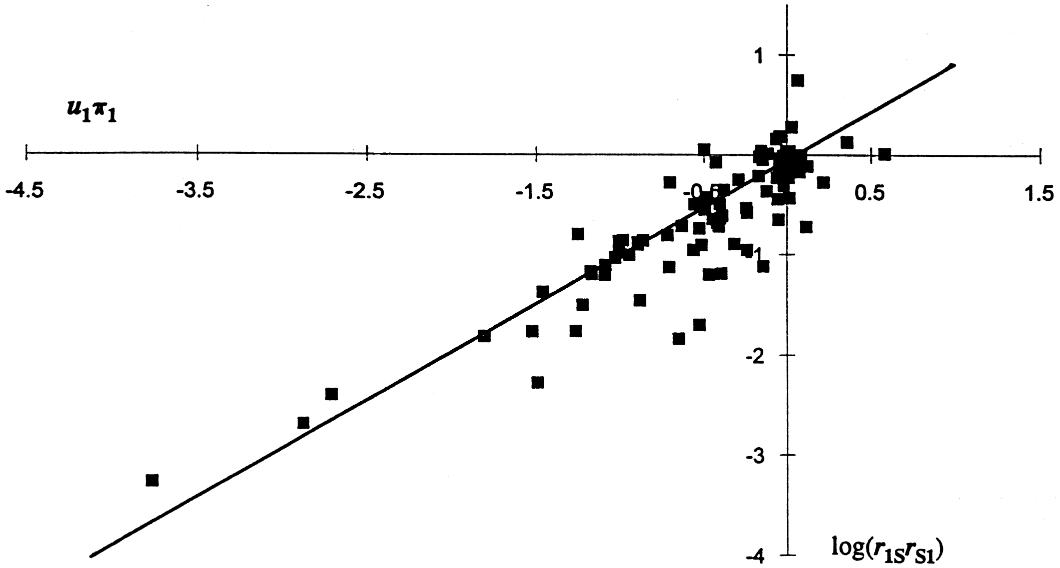

Figure 1. Test of the U, V Scheme by comparison of experimental ($\log r_{1S} + \log r_{S1}$) with $u_1\pi_1$.

monomer and its derived radical is scarcely intuitively obvious but further examination soon furnishes an explanation. If the sum of the logarithms is written as $\log(r_{1S}r_{S1}) = \log(k_{11}k_{SS}/k_{1S}k_{S1})$, one observes that three of the four velocity constants involve styrene, a monomer which is not influenced by polar factors, either through the monomer itself or the derived radical because $u_S = v_S = \pi_S = 0$. Only k_{11} is subject to polar influence, and the parameters u_1 and π_1 therefore determine the value of $r_{1S}r_{S1}$. Equation 19 is not valid if the more general formulation is used.

The Alternating Tendency

When monomer reactivity ratios were first systematically evaluated and interpreted, it was recognized by Mayo and Walling [13] that the product $r_{12}r_{21}$ constituted an inverse measure of the preference of the monomers to alternate in the copolymer, the so-called "Alternating Tendency"; the lower the value of $r_{12}r_{21}$, the greater the tendency to alternate. It is therefore of interest to examine the ability of the Revised Patterns Scheme to provide a useful estimate of the alternating tendency.

Before performing any calculation, it would not be expected that a very high degree of correspondence between calculated and experimental values of

TABLE 1. Test of Equation 19. Correlation of Experimental (log r_{1S} + log r_{S1}) with $u_1\pi_1$.

Monomer 1	r_{1S}	r_{S1}	u_1	π_1	$u_1 . \pi_1$	$\log(r_{1S}.r_{S1})$
Acrolein	0.27	0.23	-2.75	0.397	-1.092	-1.207
Acrolein, methyl	0.6	0.26	-1.65	0.436	-0.719	-0.807
Acrylamide	0.7	1.2	-1.82	0.237	-0.431	-0.076
Acrylamide, *N*-methylol	0.48	0.03	-1.41	0.463	-0.653	-1.842
Acrylamide, *N*-octadecyl	0.54	2.08	-1.56	0.321	-0.501	0.050
Acrylate, benzyl	0.2	0.494	-2.68	0.353	-0.946	-1.005
Acrylate, n-butyl	0.18	0.77	-2.22	0.443	-0.983	-0.858
Acrylate, 2-chloroethyl	0.12	0.53	-2.38	0.492	-1.171	-1.197
Acrylate, chloromethyl	0.3	0.25	-1.55	0.457	-0.708	-1.125
Acrylate, 3,4-epoxyhexahydrobenzyl	1.97	0.27	-1.95	-0.11	0.215	-0.274
Acrylate, ethyl	0.17	0.81	-1.99	0.434	-0.864	-0.861
Acrylate, methyl	0.18	0.75	-2.39	0.421	-1.006	-0.870
Acrylate, 2-nitrobutyl	0.12	0.35	-2.4	0.61	-1.464	-1.377
Acrylate, octadecyl	0.26	0.61	-3.01	0.417	-1.255	-0.800
Acrylate, octyl	0.01	0.39	-3	0.902	-2.706	-2.409

Acrylate, phenyl methyl	1.28	0.06	-0.33	0.439	-0.145	-1.115
Acrylate, di-zinc	0.9	1.1	-1.38	-0.06	0.083	-0.004
Acrylonitrile	0.04	0.38	-2.59	0.699	-1.810	-1.818
Acryloyl chloride	0.02	0.1	-3.53	0.815	-2.877	-2.699
Allyl chloride	0.04	36	-0.41	0.162	-0.066	0.158
Benzothiazole, vinylmercapto	0.42	2.6	-0.38	0.018	-0.007	0.038
Butadiene	1.4	0.57	-0.57	-0.101	0.058	-0.098
Butadiene, 1-carboxylic acid	5.55	0.08	-1.39	0.276	-0.384	-0.353
Butadiene, 2-chloro	6.91	0.038	-2.16	0.113	-0.244	-0.581
Butadiene, 1,4 -dicarboxylic acid	0.52	0.15	-2.17	0.502	-1.089	-1.108
ditto, diethyl ester	0.56	0.12	-2.72	0.433	-1.178	-1.173
Butadiene, 2-fluoro	1.67	0.22	-1.34	-0.009	0.012	-0.435
Citraconamide, *N*-methyl	0.24	0.145	-2.8	0.315	-0.882	-1.458
Crotonaldehyde	0.07	14.7	-2.07	-0.279	0.578	0.012
Crotonate, α-cyano, ethyl	0.02	0.26	-4.34	0.345	-1.497	-2.284
Crotonate, α-methoxy, methyl	0.04	18.4	-0.19	0.199	-0.038	-0.133
Crotonate, α-methyl, methyl	0.02	30.7	-0.55	0.315	-0.173	-0.212
Ethylene, tetrachloro	0.001	191	-2.56	0.162	-0.415	-0.719
Fumarate, diethyl	0.06	0.33	-4.04	0.131	-0.529	-1.703

(*continued*)

TABLE 1. (*Continued*)

Hexatriene, tetrachloro	0.85	0.123	-2.39	0.421	-1.006	-0.981
Isoprene	1.84	0.458	-0.31	-0.073	0.023	-0.074
Isopropenyl methyl ketone	0.48	0.38	-1.91	0.277	-0.529	-0.739
Itaconic acid	0.12	0.26	-2.5	0.491	-1.228	-1.506
Itaconic anhydride	0.55	0.031	-2.39	0.531	-1.269	-1.768
Maleate, diethyl	0.04	7.03	-2.5	0.199	-0.498	-0.551
Maleimide, *N*-(2-chlorophenyl)	0.021	0.025	-4.25	0.887	-3.770	-3.280
Methacrylamide, *N*-phenyl	0.88	1.24	-1.26	0.126	-0.159	0.038
Methacrylate, benzyl	0.47	0.52	-1.4	0.281	-0.393	-0.612
Methacrylate, 2-bromoethyl	0.41	0.32	-1.97	0.455	-0.896	-0.882
Methacrylate, n-butyl	0.53	0.6	-1.55	0.264	-0.409	-0.498
Methacrylate, iso-butyl	0.42	0.54	-1.43	0.315	-0.450	-0.644
Methacrylaye, 2-chloroethyl	0.3	0.37	-1.39	0.406	-0.564	-0.955
Methacrylate, glycidyl	0.5	0.415	-1.31	0.324	-0.424	-0.683
Methacrylate, methyl	0.46	0.5	-1.2	0.338	-0.406	-0.638
Methacrylate, 2,2,6,6,-tetramethyl	0.3	0.63	0.14	0.803	0.112	-0.724
Methacrylate, 3,5-dimethyladamantyl	0.63	0.89	-1.04	0.283	-0.294	-0.251
Methacrylate, phenyl	0.51	0.25	-2.22	0.144	-0.320	-0.894
Methacrylonitrile	0.33	0.38	-2.07	0.432	-0.894	-0.902

Methacryoyl acetone	1.66	0.067	-0.82	0.297	-0.244	-0.954
Methylenebutyrolactone	0.7	0.09	-1.99	0.237	-0.472	-1.201
Oct-1-ene, 6,6-dimethyl	0.271	1.93	-1.58	0.446	-0.705	-0.281
Oxazoline, 2,2-iso-propenyl	0.64	0.67	-0.98	0.127	-0.124	-0.368
Oxazoline, 2,2-iso-propenyl-4,4-dimethyl	0.68	0.55	-1.48	0.327	-0.484	-0.427
Pentadienoate, *trans*-4-ethoxy-2,4-ethyl	12.2	0.04	-0.71	0.031	-0.022	-0.312
Pyridazinone-3, 2-vinyl-6-methyl	0.85	0.9	-1.35	-0.089	0.120	-0.116
ditto, 4,5-dihydro	0.13	5.92	-0.77	-0.151	0.116	-0.114
Pyridine, 2-methyl-5-vinyl	0.85	0.7	-1.08	-0.007	0.008	-0.225
Pyridine, 2-vinyl	1.26	0.53	-0.96	-0.014	0.013	-0.175
Pyridine, 2-vinyl-5-ethyl	1.09	0.74	-0.44	0.006	-0.003	-0.093
Pyridine, 4-vinyl	0.69	0.52	-0.97	0.06	-0.058	-0.445
Styrene	1	1	0	0	0.000	0.000
Styrene., *p*-acetoxy	1.26	0.86	-0.45	-0.03	0.014	0.035
Styrene, *p*-1-(2-hydroxypropyl)	0.91	0.97	-0.59	0.071	-0.042	-0.054
Styrene, *p*-2-(2-hydroxypropyl)	0.91	0.65	-0.57	0.109	-0.062	-0.228
Triallyl citrate	0.076	20.02	-0.49	0.092	-0.045	0.182
Vinyl acetate	0.02	48	-0.54	0.315	-0.170	-0.018
Vinyl *p*-benzylmethylcarbinol	0.94	0.98	-0.64	0.069	-0.044	-0.036

(*continued*)

TABLE 1. (*Continued*)

Vinyl benzoate	0.06	31.56	-0.86	-0.031	0.027	0.277
Vinyl benzoic acid	1.029	0.282	-1.04	0.238	-0.248	-0.537
Vinyl bromide	0.054	16.6	-0.83	0.179	-0.149	-0.047
Vinyl *tert*-butyl sulfide	0.158	4.36	-0.031	-0.029	0.001	-0.162
Vinyl chloroacetate	0.03	45	1.03	0.345	0.355	0.130
Vinyl chloride	0.055	18.7	-0.92	0.128	-0.118	0.012
Vinyl chloromethyl ketone	0.507	0.127	-1.57	0.254	-0.399	-1.191
Vinyl cymantrene	0.096	2.324	-0.97	0.053	-0.051	-0.651
Vinyl dichloroacetate	0.28	20	0.72	0.088	0.063	0.748
Vinyl ethyl sulfide	0.182	5.38	0.65	-0.038	-0.025	-0.009
Vinyl ethyl sulfoxide	0.1	7.82	-1.02	0.046	-0.047	-0.107
Vinyl ferrocene	0.17	3.57	-0.12	0.149	-0.018	-0.217
Vinylidene chloride	0.1075	1.79	-1.41	0.449	-0.633	-0.716
Vinyl isocyanate	0.09	7.52	0.28	0.258	0.072	-0.170
Vinyl isothiocyanate	0.435	0.725	-1.56	0.357	-0.557	-0.501
Vinyl methyl ketone	0.32	0.29	-2.5	0.412	-1.030	-1.032
Vinyl phenyl ether	0.01	1.7	-2.23	0.685	-1.528	-1.770
Vinyl(trismethoxysiloxy)silane	0.005	25	-0.84	0.614	-0.516	-0.903

the product of two monomer reactivity ratios would be achieved because it is well known that, even the "best" experimental values (which we believe to be those recalculated and tabulated by Greenley [6, 7]) are often subject to significant experimental error. If the error in each monomer reactivity ratio is (somewhat modestly) assessed as 50%, the error in the product could be as high as 225%, if the errors in both quantities operate in the same direction (1.5 x 1.5 = 2.25). Nevertheless, the comparison is worth making.

The value predicted for $\boldsymbol{r}_{12}\boldsymbol{r}_{21}$ by the revised Patterns Scheme can be arrived at as follows. Using the form of Equation (3a) for both log $\boldsymbol{r}_{12}$ and log $\boldsymbol{r}_{21}$, the product can be written as follows:

$$\log(\boldsymbol{r}_{12}.\boldsymbol{r}_{21}) = \log \boldsymbol{r}_{12} + \log \boldsymbol{r}_{21} = \log \boldsymbol{r}_{1S} - \boldsymbol{u}_2\boldsymbol{\pi}_1 - \boldsymbol{v}_2 + \log \boldsymbol{r}_{2S} - \boldsymbol{u}_1\boldsymbol{\pi}_2 - \boldsymbol{v}_1 \qquad (20)$$

It was seen above, in the discussion of the U,V Scheme, that log $\boldsymbol{r}_{S1} = -\boldsymbol{v}_1$ and log $\boldsymbol{r}_{S2} = -\boldsymbol{v}_2$, hence,

$$\log(\boldsymbol{r}_{12}.\boldsymbol{r}_{21}) = \log \boldsymbol{r}_{1S} - \boldsymbol{u}_2\boldsymbol{\pi}_1 + \log \boldsymbol{r}_{S2} + \log \boldsymbol{r}_{2S} - \boldsymbol{u}_1\boldsymbol{\pi}_2 + \log \boldsymbol{r}_{S1}$$

but, from Equation 19, log $\boldsymbol{r}_{1S}$ + log $\boldsymbol{r}_{S1} = \boldsymbol{u}_1\boldsymbol{\pi}_1$ and log $\boldsymbol{r}_{2S}$ + log $\boldsymbol{r}_{S2} = \boldsymbol{u}_2\boldsymbol{\pi}_2$, therefore

$$\log(\boldsymbol{r}_{12}.\boldsymbol{r}_{21}) = -\boldsymbol{u}_2\boldsymbol{\pi}_1 - \boldsymbol{u}_1\boldsymbol{\pi}_2 + \boldsymbol{u}_1\boldsymbol{\pi}_1 + \boldsymbol{u}_2\boldsymbol{\pi}_2$$

or

$$\log(\boldsymbol{r}_{12}.\boldsymbol{r}_{21}) = (\boldsymbol{u}_1 - \boldsymbol{u}_2)(\boldsymbol{\pi}_1 - \boldsymbol{\pi}_2) \qquad (21)$$

Thus, the Alternating Tendency is seen to be a function only of the polarity parameters for the radicals and monomers, an extremely reasonable conclusion. Data for all the vinyl monomers in Greenley's list [6] in the 4th edition of the Polymer Handbook that have monomer reactivity ratios recorded for reaction with all five members of the Basic Monomer Set [2] are presented in Table 2 and are used to test Equation 21 in Figure 2. Although the expected scatter is apparent, the general trend of the points is good confirmation of the essential validity of Equation 19.

TABLE 2. Test of Equation 21. Correlation of Experimental log($r_{12.}r_{21}$) with (u_1 - u_2)(π_1 - π_2). In the Monomer 2 Column, the Following Abbreviations Are Used: S, Styrene; MM, Methyl Methacrylate; MA, Methyl Acrylate; MAN, Methacrylonitrile; AN, Acrylonitrile; VC2, Vinylidene Chloride; and VP2, 2-Cinyl Pyridine.

Monomer 1	u_1	π_1	**Monomer 2**	u_2	π_2	(u_{1-} u_2)	(π_1.π_2)	$\Delta u.\Delta\pi$	$r_{12}r_{21}$	log($r_{12.}r_{21}$)
						Δu	$\Delta\pi$			
Acrolein	-2.75	0.397	S	0	0	-2.75	0.397	-1.092	0.27	0.23
	-2.75	0.397	MM	-1.2	0.338	-1.55	0.059	-0.091	0.68	1.23
	-2.75	0.397	MA	-2.39	0.421	-0.36	-0.024	0.009	1.41	0.83
	-2.75	0.397	MAN	-2.07	0.432	-0.68	-0.035	0.024	0.7	1.18
	-2.75	0.397	AN	-2.59	0.699	-0.16	-0.302	0.048	1.11	0.78
Acrolein, methyl	-1.65	0.436	S	0	0	-1.65	0.436	-0.719	0.6	0.26
	-1.65	0.436	MM	-1.2	0.338	-0.45	0.098	-0.044	0.4	0.41
	-1.65	0.436	MAN	-2.07	0.432	0.42	0.004	0.002	1.25	0.45
	-1.65	0.436	AN	-2.59	0.699	0.94	-0.263	-0.247	3.1	0.15
Acrylamide, *N*-methylol	-1.41	0.463	S	0	0	-1.41	0.463	-0.653	0.48	1.55
	-1.41	0.463	MM	-1.2	0.338	-0.21	0.125	-0.026	0.7	1.62
	-1.41	0.463	MA	-2.39	0.421	0.98	0.042	0.041	1.9	1.3
	-1.41	0.463	AN	-2.59	0.699	1.18	-0.236	-0.278	2.43	0.6
Acrylate, 2-chloroethyl	-2.39	0.492	S	0	0	-2.39	0.492	-1.176	0.12	0.53

	-1.41	0.492	MM	-1.2	0.338	-0.21	0.154	-0.032	0.37	2.15
	-2.39	0.494	MA	-2.39	0.421	0	0.073	0.000	1.07	0.9
Acrylate, methyl	-2.39	0.421	S	0	0	-2.39	0.421	-1.006	0.18	0.75
	-2.39	0.421	MM	-1.2	0.338	-1.19	0.083	-0.099	0.4	2.15
	-2.39	0.421	MAN	-2.07	0.432	-0.32	-0.011	0.004	0.5	2
	-2.39	0.421	AN	-2.59	0.699	0.2	-0.278	-0.056	0.85	1.42
Acrylonitrile	-2.59	0.699	S	0	0	-2.59	0.699	-1.810	0.04	0.38
	-2.59	0.699	MM	-1.2	0.338	-1.39	0.361	-0.502	0.14	1.32
	-2.59	0.699	MA	-2.39	0.421	-0.2	0.278	-0.056	1.42	0.85
	-2.59	0.699	MAN	-2.07	0.432	-0.52	0.267	-0.139	0.43	1.67
Acryloyl chloride	-3.53	0.815	S	0	0	-3.53	0.815	-2.877	0.02	0.1
	-3.53	0.815	MM	-1.2	0.338	-2.33	0.477	-1.111	0.78	0.46
	-3.53	0.815	MA	-2.39	0.421	-1.14	0.394	-0.449	2.3	0.34
	-3.53	0.815	VC2	-1.34	0.346	-2.19	0.469	-1.027	1.12	0.5
	-3.53	0.815	AN	-2.59	0.699	-0.94	0.116	-0.109	1	1.2
Butadiene, 2-chloro	-2.16	0.113	S	0	0	-2.16	0.113	-0.244	6.91	0.038
	-2.16	0.113	MM	-1.2	0.338	-0.96	-0.225	0.216	6.33	0.08
	-2.16	0.113	MA	-2.39	0.421	0.23	-0.308	-0.071	10.4	0.06
	-2.16	0.113	VP2	-0.98	-0.014	-1.18	0.127	-0.150	5.19	0.06

(continued)

TABLE 2. (*Continued*)

Diallyl phthalate	-0.81	0.048	S	0	0	-0.81	0.048	-0.039	0.076	23.5
	-0.81	0.048	MM	-1.2	0.338	0.39	-0.29	-0.113	0.053	22.12
	-0.81	0.048	MA	-2.39	0.421	1.58	-0.373	-0.589	0.033	6.19
	-0.81	0.048	AN	-2.59	0.699	1.78	-0.651	-1.159	0.0385	3.5
Hexatriene, tetrachloro	-2.39	0.421	S	0	0	-2.39	0.421	-1.006	0.85	0.123
	-2.39	0.421	MM	-1.2	0.338	-1.19	0.083	-0.099	1.76	0.504
	-2.39	0.421	MA	-2.39	0.421	0	0	0.000	3.19	0.262
	-2.39	0.421	AN	-2.59	0.699	0.2	-0.278	-0.056	4.01	0.234
Isoprene	-0.31	-0.073	S	0	0	-0.31	-0.073	0.023	1.84	0.458
	-0.31	-0.073	MM	-1.2	0.338	0.89	-0.411	-0.366	0.64	0.25
	-0.31	-0.073	MA	-2.39	0.421	2.08	-0.494	-1.028	0.75	0.12
	-0.31	-0.073	AN	-2.59	0.699	2.28	-0.772	-1.760	0.45	0.03
Methacrylate, n-butyl	-1.55	0.264	S	0	0	-1.55	0.264	-0.409	0.53	0.6
	-1.55	0.264	MM	-1.2	0.338	-0.35	-0.074	0.026	1.66	0.9
	-1.55	0.264	VC2	-1.34	0.346	-0.21	-0.082	0.017	2.07	0.35
	-1.55	0.264	MAN	-2.07	0.432	0.52	-0.168	-0.087	0.75	0.56
Methacrylate, isobutyl	-1.43	0.315	S	0	0	-1.43	0.315	-0.450	0.42	0.54
	-1.43	0.315	MM	-1.2	0.338	-0.23	-0.023	0.005	1.18	0.77
	-1.43	0.316	MAN	-2.07	0.432	0.64	-0.116	-0.074	0.68	0.74

Methacrylate, methyl	-1.2	0.338	S	0	0	-1.2	0.338	-0.406	0.46	0.5
	-1.2	0.338	MA	-2.39	0.421	1.19	-0.083	-0.099	2.15	0.4
	-1.2	0.338	MAN	-2.07	0.432	0.87	-0.094	-0.082	0.75	0.5
	-1.2	0.338	AN	-2.59	0.699	1.39	-0.361	-0.502	1.32	0.14
Methacrylonitrile	-2.07	0.432	S	0	0	-2.07	0.432	-0.894	0.33	0.38
	-2.07	0.432	MM	-1.2	0.338	-0.87	0.094	-0.082	0.5	0.75
	-2.07	0.432	MA	-2.39	0.421	0.32	0.011	0.004	2	0.5
	-2.07	0.432	AN	-2.59	0.699	0.52	-0.267	-0.139	1.67	0.43
Oxazoline,2,2-isopropenyl	-0.98	0.127	S	0	0	-0.98	0.127	-0.124	0.64	0.67
	-0.98	0.127	MM	-1.2	0.338	0.22	-0.211	-0.046	0.99	0.69
	-0.98	0.127	MA	-2.39	0.421	1.41	-0.294	-0.415	1.99	0.24
	-0.98	0.127	AN	-2.59	0.699	1.61	-0.572	-0.921	0.52	0.13
ditto, 4,4-dimethyl	-1.48	0.327	S	0	0	-1.48	0.327	-0.484	0.68	0.55
	-1.48	0.327	MM	-1.2	0.338	-0.28	-0.011	0.003	0.82	0.53
	-1.48	0.327	MA	-2.39	0.421	0.91	-0.094	-0.086	1.3	0.46
	-1.48	0.327	AN	-2.59	0.699	1.11	-0.372	-0.413	1.83	0.24
Pyridine, 2-methyl-5-vinyl	-1.08	-0.007	S	0	0	-1.08	-0.007	0.008	0.85	0.7
	-1.08	-0.007	MM	-1.2	0.338	0.12	-0.345	-0.041	0.54	0.42
	-1.08	-0.007	MA	-2.39	0.421	1.31	-0.428	-0.561	1	0.18

(*continued*)

TABLE 2. (*Continued*)

	-1.08	-0.007	AN	-2.59	0.699	1.51	-0.706	-1.066	0.31	0.16
Pyridine, 2-vinyl	-0.96	-0.014	S	0	0	-0.96	-0.014	0.013	1.26	0.53
	-0.96	-0.014	MM	-1.2	0.338	0.24	-0.352	-0.084	0.82	0.35
	-0.96	-0.014	MA	-2.39	0.421	1.43	-0.435	-0.622	2	0.25
	-0.96	-0.014	AN	-2.59	0.699	1.63	-0.713	-1.162	0.44	0.1
Pyridine, 2-vinyl-5-ethyl	-0.44	0.006	S	0	0	-0.44	0.006	-0.003	1.09	0.74
	-0.44	0.006	MM	-1.2	0.338	0.76	-0.332	-0.252	0.68	0.39
	-0.44	0.006	MA	-2.39	0.421	1.95	-0.415	-0.809	1.32	0.18
	-0.44	0.006	AN	-2.59	0.699	2.15	-0.693	-1.490	0.43	0.04
Pyridine, 4-vinyl	-0.97	0.06	S	0	0	-0.97	0.06	-0.058	0.69	0.52
	-0.97	0.06	MM	-1.2	0.338	0.23	-0.278	-0.064	0.88	0.555
	-0.97	0.06	MA	-2.39	0.421	1.42	-0.361	-0.513	1.96	0.175
	-0.97	0.06	AN	-2.59	0.699	1.62	-0.639	-1.035	0.375	0.1
Styrene	0	0	MM	-1.2	0.338	1.2	-0.338	-0.406	0.5	0.46
	0	0	MA	-2.39	0.421	2.39	-0.421	-1.006	0.75	0.18
	0	0	MAN	-2.07	0.432	2.07	-0.432	-0.894	0.38	0.33
	0	0	AN	-2.59	0.699	2.59	-0.699	-1.810	0.38	0.04
Vinyl acetate	-0.54	0.315	S	0	0	-0.54	0.315	-0.170	0.02	48
	-0.54	0.315	MM	-1.2	0.338	0.66	-0.023	-0.015	0.05	25.6

	-0.54	0.315	MA	-2.39	0.421	1.85	-0.106	-0.196	0.03	6.46
	-0.54	0.315	MAN	-2.07	0.432	1.53	-0.117	-0.179	0.01	12
	-0.54	0.316	AN	-2.59	0.699	2.05	-0.383	-0.785	0.05	4.78
Vinyl chloride	-0.92	0.128	S	0	0	-0.92	0.128	-0.118	0.055	18.7
	-0.92	0.128	MM	-1.2	0.338	0.28	-0.21	-0.059	0.07	8.99
	-0.92	0.128	MA	-2.39	0.421	1.47	-0.293	-0.431	0.039	5.26
	-0.92	0.128	AN	-2.59	0.699	1.67	-0.571	-0.954	0.045	3.29
Vinylidene chloride	-1.41	0.449	S	0	0	-1.41	0.449	-0.633	0.108	1.79
	-1.41	0.449	MM	-1.2	0.338	-0.21	0.111	-0.023	0.23	2.29
	-1.41	0.449	MA	-2.39	0.421	0.98	0.028	0.027	0.87	0.92
	-1.41	0.449	MAN	-2.07	0.432	0.66	0.017	0.011	0.33	2.4

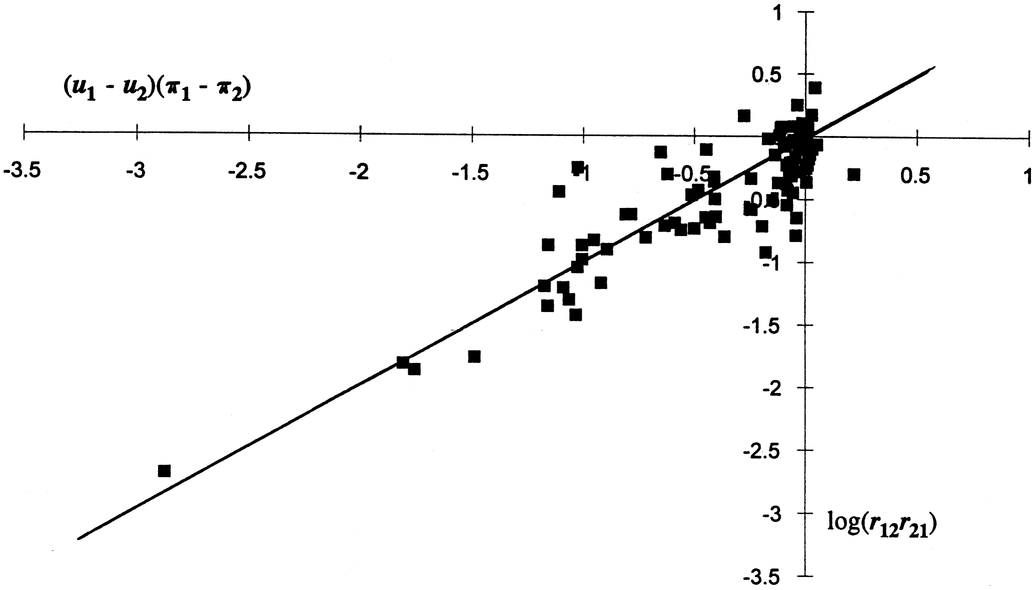

Figure 2. Test of the Patterns Formulation of the Alternating Tendency.

CONCLUSION

In the U, V Scheme, as previously presented [2], intrinsic radical reactivity is quantified by reference to the rate of reaction of the radical with styrene monomer. This is a special case of a more general approach which is described here. Although, in principle, the general procedure involves fewer assumptions, in practice much of the utility is lost. Thus, the general formulation excludes the use of the extremely convenient A,S Scheme, it does not correspond to the (experimentally substantiated) correlation of π_1 and σ_1, and it fails to lead to a simple equation describing the Alternating Tendency. It is clearly seen that it is not only convenient but also entirely satisfactory in practice to employ k_{1S} as the criterion of intrinsic radical reactivity.

ACKNOWLEDGEMENT

Dr. Cheves T. Walling has kindly provided wise criticism of the Revised Patterns Scheme, and indeed was responsible both for deriving Equation (21) and for suggesting the general formulation. His counsel is greatly appreciated, he was a pio-

neer of radical polymerization in the 1940s and he continues to contribute to its advancement today.

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Received June 15, 2000