The Prediction of Reactivity in Radical Polymerisation

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SUMMARY: Until recently, the only method available for the prediction of monomer reactivity ratios in radical polymerisation was the Alfrey-Price *Q-e* Scheme. This has now been adapted in such a way that all the scheme's undesirable features have been removed and no assumptions are involved other than the basic separation of reactivity into thermodynamic and polar components. It is then found that, provided that the copolymerisation behaviour of any given monomer with (i) styrene and (ii) acrylonitrile has been characterised, its copolymerisation with any other monomer, similarly characterised, can be predicted with much greater precision than hitherto. This procedure is called the Revised Patterns of Reactivity Scheme, or "Patterns". Unlike the *Q-e* Scheme, a parallel procedure can be applied to the prediction of transfer constants, with remarkable accuracy over a spread of transfer constant values of nine orders of magnitude. The procedure can also be applied to evaluate the reactivity of initiator radicals with monomers. A side-product of the Patterns scheme is a simple method for obtaining approximate values of the Hammett σ constant for the substituent present on the α-carbon atom of a monomer.

Introduction

One of the most important aspects of the study of copolymerisation 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 copolymerisation with monomers M_1 and M_2, this is usually written in the form known as the copolymer composition equation[1], copolymerisation equation, or copolymer equation:

$$R_p = R_m(\boldsymbol{r_{12}}R_m + 1)/(\boldsymbol{r_{21}} + R_m) \qquad (1)$$

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.

The *Q-e* Scheme

Following a perceptive (but rarely quoted) analysis of reactivity by Price[2] which highlighted the importance of polarity in radical reactions, Alfrey and Price[3] assumed that "general" (i.e.

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thermodynamic) reactivity - the converse of stabilisation - must govern reactivity in part, as it must in all chemical processes, but that there may also be a polar contribution to reactivity resulting from mutual attraction or repulsion between the two reactants. Each reactant was allocated a parameter $\boldsymbol{Q}$, denoting general reactivity, and another parameter $\boldsymbol{e}$, denoting the supposed permanent electric charge carried by that entity (radical or molecule). For reaction between a radical (species 1) and a monomer (species 2), the rate constant, $\boldsymbol{k}_{12}$, was postulated to be related to the four relevant reactivity parameters by equation 2.

$$\boldsymbol{k}_{12} = \boldsymbol{Q}_1\boldsymbol{Q}_2 \exp(-\boldsymbol{e}_1\boldsymbol{e}_2) \text{ or } \ln \boldsymbol{k}_{12} = \ln \boldsymbol{Q}_1\boldsymbol{Q}_2 - \boldsymbol{e}_1\boldsymbol{e}_2 \qquad (2)$$

[To be strictly accurate, Alfrey and Price used the symbol P to denote the general reactivity of a radical but Q will be employed here.]

Shortcomings of the *Q-e* Scheme

There are three obvious serious objections to the *Q-e* scheme: (i) permanent electric charges are presumed to exist on all the species involved; (ii) the polarity of a monomer is presumed to be identical to that of a radical bearing a terminal unit derived from that monomer; and (iii) dependence of rate constants on the relative permittivity of the medium [expected on the basis of assumption (i)] has not been observed.

Experimental determination of the two monomer reactivity ratios for a binary system does not provide an evaluation of $\boldsymbol{Q}_1$, $\boldsymbol{Q}_2$, $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$; to identify these four quantities with numerical values necessitates the allocation of essentially arbitrary values to one pair of $\boldsymbol{Q}$, $\boldsymbol{e}$ parameters. Although quite a lot has been written about this exercise[4], for present purposes it is sufficient to note that the values $\boldsymbol{Q}$ = 1.0 and $\boldsymbol{e}$ = - 0.8 have been used almost universally for styrene, despite the strange concept that a styrene molecule, e.g. in toluene solution, permanently carries 80% of an electronic charge. The arbitrary nature of the assignment of the parameters for styrene constitutes a fourth serious objection to the ***Q-e*** scheme.

The Revised "Patterns of Reactivity" Scheme

Recently, the Revised "Patterns of Reactivity" Scheme has been developed[5,6], 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**,

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

σ_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 (σ_p)[7] 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.

In the Revised Patterns Scheme[5,6], the parallel to equation (2) is equation (3).

$$\log \boldsymbol{k}_{12} = \log \boldsymbol{k}_{1S} + \boldsymbol{u}_2\sigma_1 + \boldsymbol{v}_2 \qquad (3)$$

The term log $\boldsymbol{k}_{11}$ is now subtracted from both sides to give equation (4)

$$\log \boldsymbol{r}_{12} = \log \boldsymbol{r}_{1S} - \boldsymbol{u}_2\sigma_1 - \boldsymbol{v}_2 \qquad (4)$$

Equation (4) is essentially a postulate, based on the rather modest level of success of the ***Q-e*** scheme, but it is the only feature that is assumed in the Revised Patterns treatment, and it has previously been shown[6] that the predictions made on this basis are much closer to the experimental values than are those of the *Q-e* Scheme. The procedure described here is known as the Patterns U,V Scheme.

A test of the validity of equation (4) is to plot the LHS of the rearranged form equation (5), below, against σ_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[8,9].)

$$\log \boldsymbol{r}_{12} - \log \boldsymbol{r}_{1S} = -\boldsymbol{u}_2\sigma_1 - \boldsymbol{v}_2 \qquad (5)$$

This test is performed in Fig.1 with acrylonitrile as monomer **2** and denoted by subscript "**A**", the monomers **1** being the members of the Basic Monomer Set[5], that is styrene (S), methyl methacrylate (MM), methyl acrylate (MA), methacrylonitrile (MAN) and acrylonitrile (A or AN), i.e.,

$$\log \boldsymbol{r}_{1A} - \log \boldsymbol{r}_{1S} = -\boldsymbol{u}_A\sigma_1 - \boldsymbol{v}_A \qquad (6)$$

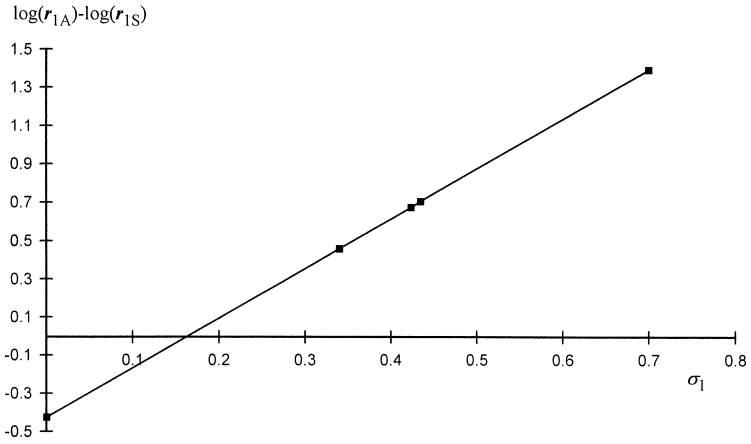

Figure 1: Test of equation (5); plot of [log($\boldsymbol{r}_{1A}$) - log($\boldsymbol{r}_{1S}$)] *versus* σ_1.

From the slope of this plot, u_A = -2.60 and, from the intercept on the ordinate axis at $\sigma_1 = 0$, $v_A = 0.42$.

If the case is now considered where monomer 2 is acrylonitrile while monomer **1** is some selected monomer, say **X**, a rearrangement of equation (6) produces a general expression for σ_X, exclusively in terms of polymerisation data.

$$\sigma_X = -(1/u_A)[\log r_{XA} - \log r_{XS} + v_A] \qquad (7)$$

Since the values of u_A and v_A are known (see above), this equation can be condensed to

$$\sigma_X = 0.385\log[r_{XA}/0.377r_{XS}] \qquad (8)$$

It thus appears that, for any monomer, one can calculate σ_X provided that we know two of the monomer reactivity ratios for the separate copolymerisations of monomer **x** with (i) acrylonitrile and (ii) styrene. This procedure thus provides a valuable 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 ionisation of substituted benzoic acids and tabulated by Shorter[10,11] on behalf of IUPAC, ***or*** one can rely exclusively on polymerisation data and employ equation (8). If the latter course is adopted, the symbol π_x is used rather than σ_x for the result in order to emphasise the difference in procedure, and the basic equation (4) is rewritten as (9), thus:

$$\log r_{12} = \log r_{1S} - u_2\pi_1 - v_2 \qquad (9)$$

In fact, where comparison is possible, σ_x and π_x are found to have virtually identical values[15].

The A,S Scheme

A condensed version[12] of the procedure, called the **A,S Scheme**, is available for circumstances in which *only* the monomer reactivity ratios for the copolymerisation of monomers **1** and **2** with styrene and acrylonitrile (respectively, the least and most polar reference monomers) 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 (10) to obtain r_{12}.

$$\log(r_{12}) = \log[(r_{1S})(r_{S2}]) - \frac{[\log(r_{AS})(r_{S2})/(r_{A2})][\log(r_{SA})(r_{1S})/(r_{1A})]}{(r_{AS})(r_{SA})] \qquad (10)$$

Further Tests 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 ($=k_{11}/k_{11}$); it was shown

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 $-\nu_1$ (see above).

$$\log r_{11} = \log r_{1S} - u_1\pi_1 + \log r_{S1} = 0 \qquad (11)$$

or

$$\log(r_{1S}r_{S1}) = u_1\pi_1 \qquad (12)$$

A plot of the left hand side of equation (12) *versus* its right hand side is presented in Fig. 2 for a total of 90 monomers, and the line of unit slope drawn thereupon corresponds to perfect agreement. While a measure of experimental error is inevitably apparent, the general trend of agreement is clear. The monomers for which data were employed are those listed in the Table of Patterns of Reactivity Parameters[13] in the 4th edition of the Polymer Handbook for which the necessary data are available; 1,2-disubstituted monomers have been excluded on account of their different structural features.

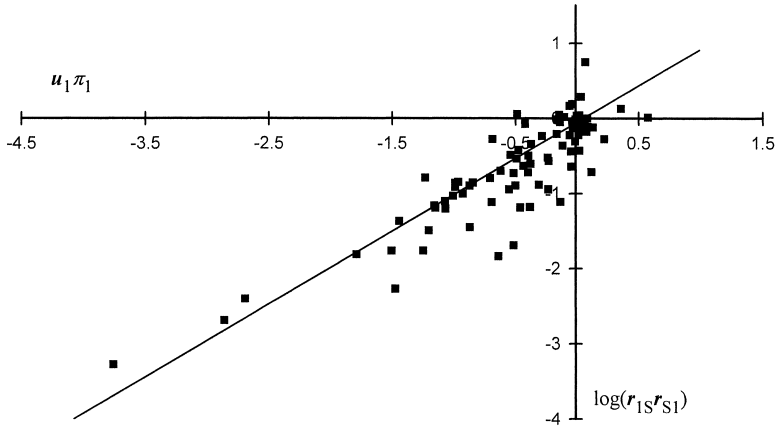

Figure 2: Test of equation (12); plot of $\log(r_{1S}r_{S1})$ *versus* $u_1\pi_1$.

The result that the sum of the logarithms of the two complementary monomer reactivity ratios for the copolymerisation of styrene with any selected monomer is given by the simple product of the polarity parameters for that 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 its derived radical because $u_S = \nu_S = \pi_S = 0$. Only k_{11} is subject to polar influence, and the parameters u_1 and π_1 therefore determine the value of $r_{1S}r_{S1}$.

The Alternating Tendency

When monomer reactivity ratios were first systematically evaluated and interpreted, it was recognised by Mayo and Walling[14] 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.

The value predicted for $r_{12}r_{21}$ by the revised Patterns Scheme can be arrived at as follows. Using the form of equation (9) for both log r_{12} and log r_{21}, the product can be written as follows.

$$\log(r_{12}.r_{21}) = \log r_{12} + \log r_{21} = \log r_{1S} - u_2\pi_1 - v_2 + \log r_{2S} - u_1\pi_2 - v_1 \qquad (13)$$

It was seen above, in the discussion of the U,V Scheme, that log r_{S1} = - v_1 and log r_{S2} = - v_2, hence

$$\log(r_{12}.r_{21}) = \log r_{1S} - u_2\pi_1 + \log r_{S2} + \log r_{2S} - u_1\pi_2 + \log r_{S1}$$

but, from equation (12), log r_{1S} + log r_{S1} = $u_1\pi_1$ and log r_{2S} + log r_{S2} = $u_2\pi_2$, therefore

$$\log(r_{12}.r_{21}) = - u_2\pi_1 - u_1\pi_2 + u_1\pi_1 + u_2\pi_2$$

or

$$\log(r_{12}.r_{21}) = (u_1 - u_2)(\pi_1 - \pi_2) \qquad (14)$$

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 in the 3rd edition of the Polymer Handbook[8] that have monomer reactivity ratios recorded for reaction with all five, or four of the five, members of the Basic Monomer Set are used to test equation (14) in Fig. 3.

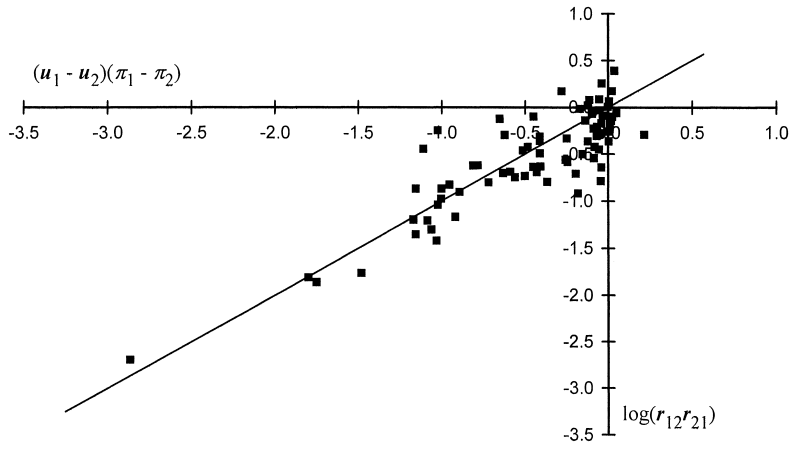

Figure 3: Test of equation (14); plot of $\log(r_{12}.r_{21})$ *versus* $(u_1 - u_2)(\pi_1 - \pi_2)$.

Although the expected scatter is apparent, the general trend of the points is good confirmation of the essential validity of equation (14) and shows that Patterns provides a good approximation to the alternating tendency.

Application of the Revised Patterns Schemes to Transfer Reactions

In the case of a transfer reaction, a derivation parallel to that leading to equation (9), produces the following result[5].

$$\log(1/\boldsymbol{C_2})_1 = \log(\boldsymbol{r_{1S}}) - \boldsymbol{u_2}\pi_1 - \boldsymbol{v_2} \qquad (15)$$

which evaluates the *reciprocal* of the logarithm of a transfer constant $(\boldsymbol{C_2})_1$ for reaction of a radical (species 1) with a transfer agent (species 2), i.e. it produces $\log (1/\boldsymbol{C_2})_1$, because the parameter $\boldsymbol{k_{11}}$ [= $(\boldsymbol{k_p})_1$] occurs in the *numerator* of a monomer reactivity ratio but in the *denominator* of a transfer constant. [Here, $\boldsymbol{u_2}$ and $\boldsymbol{v_2}$ refer to the transfer agent (species 2)].

Application of the Patterns U,V Scheme to Transfer

Rearrangement to the form of equation (16),

$$\log(1/\boldsymbol{C_2})_1 - \log(\boldsymbol{r_{1S}}) = - \boldsymbol{u_2}\pi_1 - \boldsymbol{v_2} \qquad (16)$$

shows that a plot of $[\log(\boldsymbol{C_2})_1 + \log(\boldsymbol{r_{1S}})]$ *versus* π_1 should be linear with slope $\boldsymbol{u_2}$ and ordinate intercept $\boldsymbol{v_2}$. Application of this procedure, using the members of the Basic Monomer Set as the monomer **1**, gives the $\boldsymbol{u_2}$ and $\boldsymbol{v_2}$ values for a number of important transfer agents. The values of the parameters so derived can be fed back into equation (16), with $\log(\boldsymbol{r_{1S}})$ and π_1, to calculate $(\boldsymbol{C_2})_1$ and so to test for internal consistency. Omitting the anomalous data for the methyl acrylate/copper(II) chloride system, the mean discrepancy[6] is 56%.

Application of the Patterns A,S Scheme to Transfer

Beginning with equation (16), examination of the particular cases where monomer **1** is styrene or acrylonitrile leads to the following two relationships.

$$\log(\mathbf{C_2})_S = \boldsymbol{v_2}$$

$$\boldsymbol{u_2} = [\log(\boldsymbol{r_{AS}}) + \log(\mathbf{C_2})_A - \log(\mathbf{C_2})_S]/\pi_A$$

Hence, by substitution of these results into equation (16), the following relation is found.

$$\log(\mathbf{C_2})_1 = \log[(\mathbf{C_2})_S/(\boldsymbol{r_{1S}})] + (\pi_1/\pi_A)\{\log[(\boldsymbol{r_{AS}})(\mathbf{C_2})_A/(\mathbf{C_2})_S]\} \qquad (17)$$

Since $\pi_A = 0.701$ and $\boldsymbol{r_{AS}} = 0.04$, this can be reduced to equation (18).

$$\log(\mathbf{C_2})_1 = \log[(\mathbf{C_2})_S/(\boldsymbol{r_{1S}})] + (1.43\pi_1)\{\log[0.04(\mathbf{C_2})_A/(\mathbf{C_2})_S]\} \qquad (18)$$

When applied to transfer reactions with either styrene or acrylonitrile as the monomer, this equation necessarily reduces to a trivial form, and the test of its validity is its use for reactions of other monomers for which the necessary characteristic quantities are known. With respect

to the same monomers and transfer agents as in the previous section, the results obtained correspond to a mean discrepancy[6] generated in this procedure (not counting the necessarily accurate "predictions" for the reactions of styrene and acrylonitrile, and omitting data for the methyl acrylate/copper(II) chloride system) of 79%.

Summary of Results for Transfer Reactions

Both the U,V Scheme and the A,S Scheme estimate transfer constants to much better than an order of magnitude, indeed the mean discrepancies reported above are, respectively only 56 and 79%. If these figures seem to be unacceptably large, it should be borne in mind that the values of the transfer constants involved are spread over a range of ***nine orders of magnitude***, from 1.2×10^{-5} for styrene and toluene to 10300 for styrene and copper (II) chloride; the discrepancy of 56% in the U,V Scheme then appears to be rather modest.

The Reactivity of Initiator Radicals

If we now consider equation (9) and, as a separate reaction, the copolymerisation of monomers **1** and **3**, the parallel equation is

$$\log r_{13} = \log r_{1S} - u_3.\pi_1 - v_3 \qquad (19)$$

The ratio of rates of the reactions of species 1 with 2 and 3 is then derived by subtraction of equation (19) from equation (9), thus.

$$\log r_{12} - \log r_{13} = - u_2.\pi_1 - v_2 + u_3.\pi_1 + v_3 \qquad (20)$$

i.e.
$$\log (r_{12}/r_{13}) = - \pi_1(u_2 - u_3) - (v_2 - v_3) \qquad (21)$$

Remembering that $r_{12} = k_{11}/k_{12}$ and $r_{13} = k_{11}/k_{13}$, we arrive at the result:

$$\log (k_{12}/k_{13}) = \pi_1(u_2 - u_3) + (v_2 - v_3) \qquad (22)$$

It is thus found[15] that the ratio of the rates at which the initiator radical (1) reacts with the monomers (2 and 3) is given by a simple relationship involving the polarity parameter of the radical (π_1) and the u and v parameters of the two monomers.

A particularly simple situation exists if styrene is chosen to be monomer **3** because we then have $u_3 = v_3 = 0$, and equation (22) becomes (23).

$$\log (k_{12}/k_{1S}) = \pi_1.u_2 + v_2$$

or
$$\log (k_{12}/k_{1S}) - v_2 = \pi_1.u_2 \qquad (23)$$

Fig. 4 shows a plot of $[\log (k_{12}/k_{1S}) - v_2]$ *versus* u_2 for the 2-cyano-2-propyl radical, the radical obtained by decomposition of azo(bis-isobutyronitrile). The slope gives the value of π_1 for this radical (+0.347), and this can then be used in calculations of the relative reactivity of the radical with any two monomers of interest by means of equation (22).

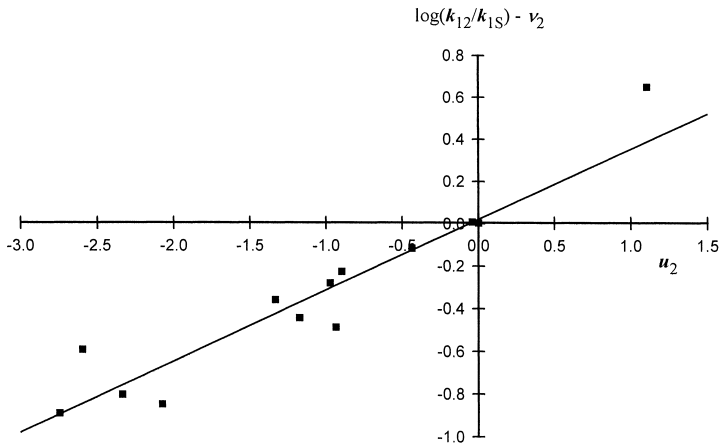

Figure 4: Test of equation (23); plot of [log (k_{12}/k_{1S}) - ν_2 *versus* u_2.

Conclusions

The Patterns Scheme is a great improvement on the ***Q-e*** Scheme, both in principle and in practice. It provides a quantitative measure of radical, monomer, and transfer agent reactivity, and offers a basis for the analysis of the reactions of initiator radicals.

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