THE POLARITY OF POLYMER RADICALS

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ABSTRACT
The main theories of radical reactivity are reviewed and compared. It is shown
that the 'Patterns' treatment remains the only approach to avoid assignment
of arbitrary standard parameters of reactivity.

The polarity of polymer radicals has engaged the attention of chemists
for a full twenty five years so that any review of the subject must, if it is to be
complete, include some material which many will regard as ancient history.
In fact, in various ways modern approaches to the subject are always subject
to comparison with the Alfrey–Price Q–e scheme[1,2] of 1946–47 so it will be as
well to begin with a brief statement of the basic problem and the first solution
to it.

Why is it necessary to take polarity into consideration in discussing the
reactivity of radicals in polymerization reactions, frequently carried out in
solvents of low dielectric constant? If polar effects were negligible radicals
would be reactive or unreactive according to the level of delocalization of
their unpaired spin so that it would be possible to draw up an unambiguous
list of radicals in order of reactivity, one which would apply to all substrates.
The failure of this proposition in practice is borne out by reference to only
two radicals, polystyrene (PS) and polyacrylonitrile (PAN), in their reactions
with a few substrates. Inspection of *Table 1* shows that not only is a statement
that 'the PS radical is n times more reactive than the PAN radical' invalid but
that one cannot say, in general, that one is more reactive than the other:
towards ferric chloride the PS radical is the more reactive by a factor of 100
but towards triethylamine the PAN radical is more reactive by a factor of
5 000[3].

Table 1. Relative reactivities of radicals derived from styrene (S) and acrylonitrile (AN)

	Substrate				
	Ferric chloride	Acrylonitrile	Vinyl chloride	Styrene	Triethylamine
Reactivity ratio for S·/AN·	100	2	0.05	0.002	0.0002

This single fact belies the fable, still found, that radicals are indiscriminate
in their tendency to attack any molecule which they encounter: while

reactivity is, on the whole, at a high level, it is plain that the degree of selectivity which is deployed is high, and the only reasonable explanation is that the transition states for radical reactions can be strongly influenced by contributions in which charge separation takes place and which are therefore dependent upon the polar character of both substrate and radical. It remains to formulate an expression for a rate constant based on parameters representing the 'general reactivity' (i.e. lack of delocalization) of the radical and its polarity.

The Q–e scheme of Alfrey and Price makes the assumptions that:

(i) general reactivity of reactants can be denoted by Q factors;
(ii) polar properties of reactants can be denoted by e factors;
(iii) for a given monomer and its derived radical the e values are identical;
(iv) a rate constant will be related to these factors by the equation

$$k_{RM} = Q_R Q_M e^{-e_R e_M}$$

or
$$\log k_{RM} = \log Q_R + \log Q_M - e_R e_M$$

A reactivity ratio will then be given by

$$r_1 = (Q_1/Q_2)e^{-e_1(e_1 - e_2)}$$

The model underlying this treatment assumes electrostatic interactions between permanent charges on radical and monomer. No-one would support that idea these days and it is therefore easy to dismiss the Q–e scheme as without serious foundation, but the fact remains that, regarded as a purely empirical exercise, it achieves a remarkable degree of success, so much so that it may be too late to expect it to be superseded by a better treatment with firmer foundations.

It is necessary, in view of what comes later, to dwell for a moment on the fact that the allocation of individual Q and e values depends upon an arbitrary assignment of two such parameters, and that the reference points chosen were $Q = 1.0$, $e = -0.8$ for styrene. Kawabata, Tsuruta and Furukawa[4] recalculated Q values after changing the styrene e parameter to 0.00 and discussed the effect on Q values in general.

Very early on Wall[5] had suggested modifying Q–e to Q–e–e^* by allowing different polar parameters for conjugate monomer–radical pairs but, of course, there are further problems in assignment of a reference e^* value and this scheme, although superior in terms of accuracy, did not catch on. (Wall's arguments were based on an analysis of reactivity ratio data for dienes which did not fit the Q–e scheme at all well.) A completely fresh attempt at a treatment of radical reactivity which avoids any arbitrary assignment of reference values was advanced in 1958 by Bamford, Jenkins and Johnston[3, 6–8], according to whom an individual rate constant for reaction between a radical and a substrate is given by

$$\log k = \log k_{3,T} + \alpha\sigma + \beta$$

where $\log k_{3,T}$ is the (measured) chain transfer constant for reaction of the radical with toluene, σ is the Hammett para sigma constant (determined in classical fashion) for the substituent on the carbon atom bearing the unpaired spin and α,β are substrate parameters, experimentally determined by reaction
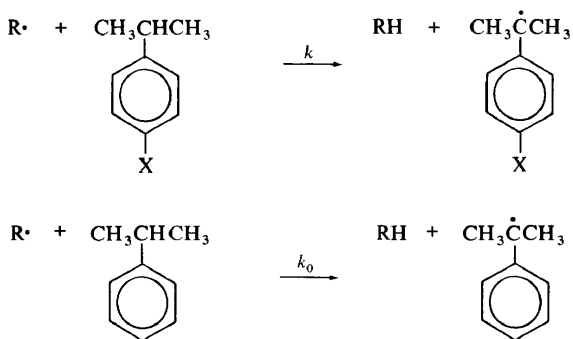
of the substrate with a series of calibrated radicals, that is radicals of known $k_{3,T}$ and σ. This scheme was derived from a collection of graphs which displayed patterns of reactivity points and is conveniently known as the 'Patterns' treatment.

'Patterns' successfully eliminates the need for any arbitrary element and it also deals with propagation and transfer reactions alike. A formal comparison of the $Q-e$ and Patterns treatments[3] reveals a basic similarity but a most important distinction, corresponding to allocation of separate polar parameters to radical–monomer pairs. It therefore represents an advance on $Q-e$ in the same sense as $Q-e-e^*$ but with the invaluable advantage that its basis rests upon experimentally determined reference data devoid of arbitrary assignment. To summarize the use of the Patterns treatment, Figure 1 shows how the order of radical reactivity is expected to depend upon the polarity of the substrate, and comparison with Table 1 demonstrates that the data therein are in excellent accord with expectation.
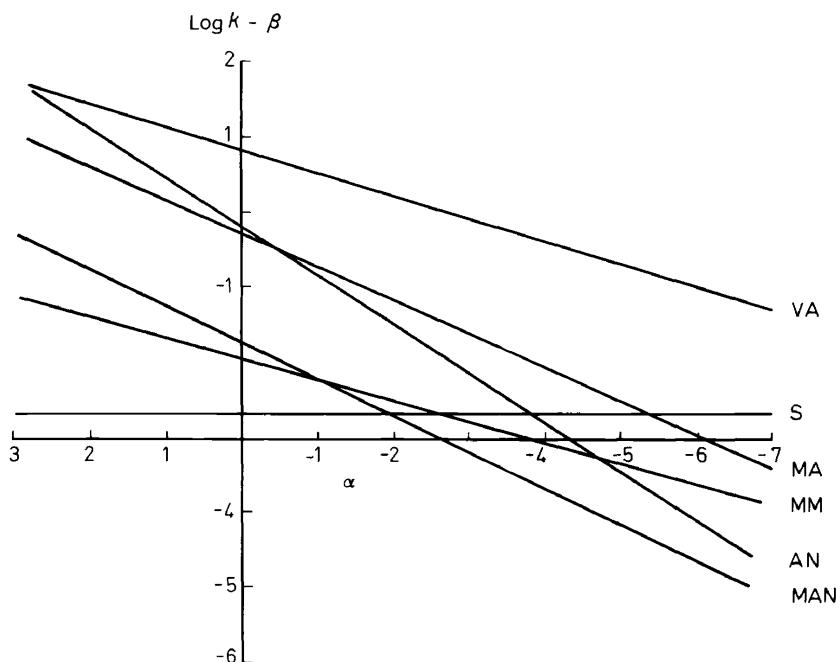
Figure 1. Relative radical reactivity as a function of substrate polarity

An alternative formulation which includes both resonance and polar terms has been put forward by Yamamoto[9] and developed by Yamamoto and Otsu[10]. Essentially, this treatment is concerned with chain transfer processes with aromatic substrates in which a comparison is made between the rates of reaction of a substituted and the unsubstituted transfer agent with a standard radical (styrene or methyl methacrylate)

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$$R\cdot \; + \; CH_3CHCH_3 \qquad\qquad RH \; + \; CH_3\dot{C}CH_3$$

$$\xrightarrow{\ k\ }$$

(benzene ring with substituent X) (benzene ring with substituent X)

$$R\cdot \; + \; CH_3CHCH_3 \qquad\qquad RH \; + \; CH_3\dot{C}CH_3$$

$$\xrightarrow{\ k_0\ }$$

(benzene ring) (benzene ring)

The equation proposed is

$$\log k = \log k_0 + \rho\sigma + \gamma E_R$$

where the σ is the Hammett parameter for the substituent group in the cumene (in this case) and E_R is a resonance parameter for the same moiety. ρ and γ are essentially coefficients which denote the relative weights to be attached to the polar and resonance contributions to the value of the rate constant. The problem arises of determining the E_R values, and Yamamoto's solution is to regard reaction with a styrene radical as a standard for which $\rho = 0$ and $\gamma = 1.0$. This seems to be quite arbitrary so that one is nearer to the Q–e than to the Patterns situation.
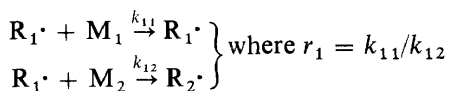
Once a list of E_R values has been obtained to complement the σs, data on the rates of other reactions can be analysed by a suitable plot to obtain the ρ and γ values. In practice this appears to mean adjusting γ to obtain the best linear plot of $\log (k/k_0)$ versus σ and deducing ρ from the slope of this plot. The treatment of several reactions in this way seems to demonstrate that γ is usually close to unity: the corresponding ρ values can be surprising, for example, for reaction with cumenes the ρ value is 0.7 for the polystyrene radical and 0.03 for the polymethylmethacrylate radical, indicating that polar contributions are much stronger in the former case. This is certainly in clear contrast to the Patterns interpretation of the characters of these two radicals.

The arbitrary character of the assignment of basic values has been mentioned above: a further shortcoming of this treatment is that it only appears to lend itself to reactions involving aromatic substrates so that it cannot be used for more than a very small portion of the available poly-merization data.

The most recent work in the field is that of Hoyland[11] who has tackled the problem in two ways, of which the first attempts to relate polarity to the electronegativity (in the Pauling sense) of the radicals and monomers. The general reactivity is similarly related to the relative localization energy for the monomer–radical pair and Hoyland then postulates that the reactivity ratio r, in a copolymerization is given by the equation

$$\log r_1 = L(2) - L(1) + \left| X_R(1) - X_M(1) \right| - \left| X_R(1) - X_M(2) \right|$$

Here $L(1)$ denotes the localization energy for monomer-radical 1 and $X_M(1)$ and $X_R(1)$ are the electronegativities of monomer 1 and radical 1 respectively. This, of course, corresponds to the competition between the two following reactions:

$$\left. \begin{array}{l} R_1{}^{\cdot} + M_1 \xrightarrow{k_{11}} R_1{}^{\cdot} \\ R_1{}^{\cdot} + M_2 \xrightarrow{k_{12}} R_2{}^{\cdot} \end{array} \right\} \text{where } r_1 = k_{11}/k_{12}$$

Hoyland's equation implies that one would write for an individual specific velocity constant

$$\log k_{RM} = L(R) - L(M) + X_R - X_M + \text{constant}$$

To put figures to the individual L and X values, Hoyland took known reactivity ratio data for five monomers (styrene, methyl acrylate, methyl methacrylate, 2-vinylpyridine and 4-vinylpyridine) and computed the best values of the various $[L(2)-L(1)]$ and $[X_R-X_M]$ terms. Attribution of numerical values of L and X parameters then depends on the arbitrary assignment of L and X_R for one of the monomers, $L = 0$ and $X_R = 0$ being selected for styrene. When the L and X values for the five primary monomers had been determined, data for another twelve were processed by computer to obtain the best fit with experimental reactivity ratios.

It is concluded that the results accord well with experiment, except for systems in which acrylonitrile is a component.

It seems that the following criticisms can be levelled against this method of tackling reactivity:
(1) An arbitrary assignment of parameters for a standard monomer is required.
(2) The five primary monomers are not ideally chosen since three of them, 2-vinylpyridine, styrene and 4-vinylpyridine are too similar in character.
(3) It would be better to select acrylonitrile as one of the primary monomers as it has the most polar single substituent; any other choice involves an implicit extrapolation to account for the behaviour of acrylonitrile and may therefore (as found) fail satisfactorily to account for it.

Hoyland's second treatment alternatively employs the concept of charge transfer so that the charge transfer energy ΔE_{CT} (R.M.) for reaction of radical R with monomer M is a factor which contributes to the specific velocity constant along with the localization energy as before. We then have

$$\log r_1 = L(2) - L(1) + \Delta E_{CT}(1,2) - \Delta E_{CT}(1,1)$$

This procedure requires a rather more elaborate analysis than his electronegativity approach but an arbitrary reference value for one of the E terms is required and the 'best values' of the parameters are derived as before, and again the systems containing acrylonitrile are exceptions to the general good agreement with experiment.

As might be expected, Hoyland finds a close correlation between X_R, X_M and some of his E values. In short, the two approaches are equivalent for practical purposes.

Dr Hoyland has provided a very useful comparison of the accuracy of all the schemes discussed here, except Patterns. The basic $Q-e$ scheme and the

Hoyland charge transfer model *without* the localization parameters are rather poor but the three parameter $Q-e-e^*$ model is significantly better, and both the Hoyland schemes (electronegativity and charge transfer) are very much better still. By including a fourth parameter the value of the models becomes very high but, of course, this is only natural in view of the decreasing gap between the number of equations and the number of unknowns. It should be clear from the foregoing that all these methods require arbitrary attribution of standard parameters and really only differ in whether one chooses to work in terms of two, three or four parameters.

It remains to assess the accuracy of the Patterns scheme by the same standard, and this work is currently in hand. However, one may observe in conclusion that the Patterns scheme alone has the advantages of using experimental measures of radical general reactivity and polarity, and of treating propagation and transfer reactions with equal facility.

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