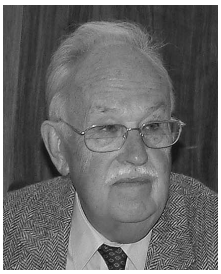

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editors

REACTIVITY IN CONVENTIONAL RADICAL POLYMERISATION

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Introduction

For the last 10 years or so, interest in radical polymerisation has mainly been focussed on techniques involving additives which form complexes with polymer radicals reversibly, producing systems with novel properties, such as narrow molecular-weight distributions[1]. The IUPAC-recommended name for this phenomenon is Controlled Reversible-Deactivation Radical Polymerization. Nevertheless, conventional methods of radical polymerisation continue to be employed for an enormous industrial output of plastics, so the mechanisms of the reactions responsible for these well-known processes remain of serious interest, especially at the research level. These mechanisms will be the main concern of the present paper.

Reactivity in conventional radical polymerisation is principally concerned with reactions between monomers or transfer agents (jointly termed "s*ubstrates*"), on the one hand, and radicals on the other. Radical polymerisation is a chain reaction but the word "chain" is confusingly used in two different ways: it can refer to the *kinetic chain*, *i.e.*, the nature of the mechanism, and it can also mean the *polymer molecule* which is the end-product. It is therefore always necessary to check whether it is a kinetic chain or a molecular chain which is being discussed. There is also the question of interactions between radicals but these are diffusion-controlled processes, which will be discussed only briefly here.

The basis for the study of reactivity in radical polymerisation was laid in the 1940s (ref.[2]), and no significant development occurred until about 1960, when a tentative revision was attempted[3]. But in the 1990s (50 years after the initial work in the field) a major advance was made which improved the accuracy of prediction of radical polymerisation reactivity to a great extent[4]. To appreciate the present position, it will be necessary to begin by reviewing, briefly, the early work in order to provide an adequate background.

The monomers mentioned above are typically mono- or di-substituted ethenes (ethylenes) which can be represented by the formulae CH_2=C(H)Y and CH_2=C(Y)Z, respectively. The group Y may be one of many things; a phenyl ring (as with styrene), an acid or ester residue (as in the case of methyl acrylate), a cyano group (for acrylonitrile), *etc.*; Z is usually, but not necessarily, a methyl or other alkyl group.

To establish the symbolism usually used to describe radical polymerisation, let us consider the simplest case, the polymerisation of a single monomer or *homopolymersation*.

Radicals have to be generated to initiate the process; the action of heat or light or high-energy radiation on monomer molecules occasionally causes initiation but, in by far the majority of instances, a substance (the *initiator*) is added which undergoes fission as a result of heat or light, generating *primary radicals*, *i.e.*, radicals which do not contain units derived from the monomer. Primary radicals add to monomer molecules to produce *polymer radicals,* which add to (typically a great many) more monomer molecules; interaction between two polymer radicals or between one polymer radical and a molecule of a transfer agent brings the polymer-building process to an end. It is assumed that the reactivity of a polymer radical is independent of the number of monomer units incorporated.

The Propagation Reaction

The heart of the polymerisation process is the propagation step, in which a polymer radical reacts with a monomer molecule (M) to produce a new polymer radical containing one more monomer unit than its predecessor, thus:

$$X_n + M \rightarrow X_{n+1}$$

where X_n is actually $\sim CH_2 — C^*(H)Y$ in which the symbol ~ (to the left of the formula) denotes the remainder of the structure of the polymer radical, *i.e.*, all the monomer units already incorporated (the number of which is represented by the subscript n), plus an end-group derived from the initiation process, and C* indicates the site of the unpaired electron on the new radical. Obviously, this is kinetically a chain reaction, propagated by radicals with one radical consumed and another formed in each step.

Sooner or later the kinetic chain is brought to an end by *either* termination

$$X_n + X_m \rightarrow P_{n+m} \text{ (combination) or } P_n + P_m \text{ (disproportionation)}$$

or by radical transfer with a transfer agent. Transfer agents are compounds that can donate an atom to a polymer radical, thus terminating the growth of that molecule but liberating a new small radical in the process. If tetrachloromethane is chosen as the transfer agent, the transfer process can be represented by the equation

$$X_n + CCl_4 \rightarrow X_nCl \text{ (or } P_n) + CCl_3$$

As the number of radicals does not change as a consequence of a reaction of this type, the rate of polymerisation is unaffected.

In the early years of polymerisation studies, it was assumed that radicals were such reactive bodies that they would react indiscriminately with any molecule they encountered but, as will be seen presently, this is a completely false view; radicals display very significant selectivity towards substrates, and this is the basis for quantitative studies of reactivity in radical polymerisations.

Homopolymerisation

If a monomer M polymerises by a radical mechanism initiated by the homolytic breakdown of an initiator C, the conventional reaction scheme for the chain process is as follows, where X_n represents a polymer radical and R· a primary radical (derived directly from the breakdown of the initiator). The component reactions, with their rate constants, are as set out below.

$$C \rightarrow 2R\cdot$$
$$R\cdot + M \rightarrow X_1 \qquad k_i$$
$$X_n + M \rightarrow X_{n+1} \qquad k_p$$
$$X_n + X_m \rightarrow \text{Polymer} \qquad k_t$$

If the rate of initiation = I, the rate of reaction is readily shown to be

$$-d[M]/dt = k_p[M](I/k_t)^{1/2}$$

By measuring the rate of reaction, it is a simple matter to evaluate $k_p/(k_t)^{1/2}$ but the separate determination of k_p and k_t has only recently become a relatively straightforward matter. Although it was, in principle, possible to determine k_t independently, e.g., by the rotating sector[5] or spatially intermittent illumination[6] techniques, few such determinations were made until the situation was revolutionised by the work of Olaj and his colleagues[7], who have shown how k_p can be determined from size-exclusion chromatography studies on the polymer formed. Although one would expect a knowledge of the absolute values of the separate rate constants to be required for an analysis of reactivity, it turns out (as will be seen below) that a great deal can be deduced from *relative reactivities*.

The word "reactivity" has been used above qualitatively but it is necessary to be more specific about what this word means in the present context. In an absolute sense, it means determining the values of the individual rate constants in the kinetic scheme above. It is then possible to make quantitative comparisons to establish the order of reactivity for a given type of participating species, monomer or polymer radical.

Some useful information about reactivity can now be obtained from studies of homopolymerisations but the amount of data available so far is not sufficient for extensive investigation of the controlling factors. By far the most prolific source of reactivity data is copolymerisation; even though this yields assessment of only *relative reactivity*, usually expressed in terms of so-called *monomer reactivity ratios* (defined below), it has provided the basis for a wide-ranging examination of reactivity in polymerisation.

Copolymerisation and the Copolymer Composition Equation

In 1944, three papers were published independently by Mayo & Lewis[8], Wall[9], and Alfrey & Goldfinger[10], all seeking to establish the relationship between the composition of a binary mixture of monomers (M_1 and M_2) and that of the resulting copolymer. An assumption implicit in their derivations was that the reactivity of a polymer radical depends only on the nature of its terminal unit, and for this reason the group of four propagation reactions represented in this scheme is known as the *Terminal Model*. Each propagation step has its own velocity constant k_{ij}, where i denotes the nature of the terminal unit on the radical while j identifies the monomer; thus, k_{12} is the velocity constant for the addition of a radical terminating in a unit derived from M_1 to a molecule of M_2. The four possible propagation steps in a binary copolymerisation (*i.e.,* a reaction involving two monomers) are the following.

$$\sim X_1 + M_1 \rightarrow \sim X_1 \qquad k_{11}$$
$$\sim X_1 + M_2 \rightarrow \sim X_2 \qquad k_{12}$$
$$\sim X_2 + M_1 \rightarrow \sim X_1 \qquad k_{21}$$
$$\sim X_2 + M_2 \rightarrow \sim X_2 \qquad k_{22}$$

The kinetic analysis of such a process is usually based on the assumption of the rapid attainment of a constant concentration of propagating radicals due to a balance being reached between the formation of radicals from the initiator and the bimolecular radical termination.

It is a simple matter to deduce, on the basis of this stationary-state assumption, that the relative rates of consumption of monomers M_1 and M_2 are given by the following equation.

$$-d[M_1]/-d[M_2] = [[M_1]\{r_{12}[M_1]+[M_2]\}]/[[M_2]\{r_{21}[M_2]+[M_1]\}] \quad (1)$$

where $r_{12} = k_{11}/k_{12}$ and $r_{21} = k_{22}/k_{21}$. The parameters r_{12} and r_{21} were originally called *monomer reactivity ratios* by Mayo & Lewis[8], but they are now usually known simply as *reactivity ratios*. Equation (*1*) is the classical *copolymer composition equation* because the ratio $-d[M_1]/-d[M_2]$ (denoted below by F) corresponds to the molar composition of the copolymer being formed instantaneously from a monomer mixture containing molar concentrations $[M_1]$ and $[M_2]$ of the components. By dividing the numerator and denominator of the right-hand side of equation (*1*) throughout by $[M_2]$, one obtains the ratio of the molar quantities of monomer units of types 1 and 2 in the copolymer as a function of the ratio $[M_1]/[M_2]$ ($=f$) in the monomer mixture, thus:

$$F = f(r_{12}f+1)/(r_{21}+f) \quad (2)$$

The clue to the understanding of behaviour in the system thus resides in the values of the two monomer reactivity ratios. Laboratories interested in this field therefore set about the task of studying radical copolymerisation systems in order to determine the monomer reactivity ratios.

Copolymerisation does not provide the list of absolute rate constants which would be ideal for the analysis of reactivity but it nevertheless furnishes a wealth of data about relative reactivities and this, as explained below, is sufficient for the main purpose. If absolute rate constants for propagation for some monomers are available, many others can be calculated from reactivity ratios.

A most valuable critical tabulation of the known reactivity ratios has been compiled by R. Z. Greenley[11]; this constitutes a library of data that can form a uniform basis for every chemist interested in studying copolymerisation.

The Basic Monomer Set and the Basic Set of Monomer Reactivity Ratios

In order to arrive at a quantitative picture of the reliability of methods for calculating monomer reactivity ratios, it is useful first to define a "Basic Monomer Set" of reliable experimental data. Thus, the following five monomers were selected for particular study: styrene (S); methyl methacrylate (MM); methyl acrylate (MA); methacrylonitrile (MAN); and acrylonitrile (AN). With the exception of one combination, these monomers have been copolymerised in all possible pairings for the determination of the reactivity ratios. For the sake of consistency, the figures quoted here are based on Greenley's data.

The Order of Radical and Monomer Reactivities

As mentioned above, it was understood by the 1940s that radicals and monomers did not fall into simple sequences of reactivity; it became clear that reactivity depended, at least partially, on an interaction specific to each radical/substrate pair. Since the *monomer reactivity ratio* $r_{12} = k_{11}/k_{12}$, the order in which monomers react with a given radical is easily established by reference to r_{12} values, because the sequence of k_{12} values is clearly the same as that of $(r_{12})^{-1}$, k_{11} being constant for a given radical. Within the Basic Monomer Set, the r_{12} values show that the broad general descending sequence of monomer reactivity is S > MM > MAN > AN > MA but, towards styrene radicals, the least reactive monomer is styrene itself.

To deduce a similar sequence of reactivity for a variety of radicals towards a given substrate is not so simple, because each radical has its own k_{11} value, and it is necessary to take this into account in calculating k_{12} from r_{12}. Using the following values of k_{11}/l mol^{-1} s^{-1} for 60 °C: S, 343; MM, 828; MA, 19000; MAN 56; AN, 2458, the general descending order of reactivity of the polymer radicals is MA > AN > MM > S > MAN. The values of most of these rate constants were determined a considerable time ago but the development of the pulsed laser has encouraged recent re-evaluations of k_{11} for styrene and methyl acrylate to be made, with the results quoted above.

The *Q-e* Scheme

As early as 1946 (ref.[2]), Charles Price, basing his deductions on the data of Mayo & Lewis[8] and of Alfrey, Merz and Mark[12], was able to conclude that it was not a straightforward matter to codify the reactivity of monomers in radical polymerisation. It was already clear that, while some monomers that undergo homopolymerisation would also readily engage in copolymerisation, others would not; it was also seen that some monomers that would *not* homopolymerise to any appreciable extent would copolymerise without difficulty. Such observations led Price to conclude that the polarity of the double bond in the monomer, arising from the influence of the substituents, Y and Z, was an important factor in deciding the outcome. In fact, Lewis, Mayo and Hulse[13] had already observed that "there may be a general order of activity of monomers towards radicals which is complicated by the tendency of some pairs to alternate in copolymerisation". It was the "alternating tendency", as it became known later, that focussed attention on the importance of polarity.

A year after the perceptive (but rarely quoted) analysis of reactivity by Price[2], which highlighted the importance of polarity in radical reactions, Alfrey and Price[14] put

Price's ideas into semi-quantitative, if empirical, form by assuming that, while "general" (*i.e.* thermodynamic) reactivity – the converse of stabilisation – governs reactivity in part (as it must in all chemical processes), there may also be a polar contribution to reactivity resulting from mutual attraction or repulsion between the two reactants, which was attributed to permanent electric charges. Each reactant was allocated a parameter, Q, denoting general reactivity and another parameter, 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, k_{12}, was postulated to be related to the four relevant reactivity parameters by the equation below.

$$k_{12} = Q_1 Q_2 \exp(-e_1 e_2)$$

or $$\ln k_{12} = \ln Q_1 + \ln Q_2 - e_1 e_2$$

Thus, the monomer reactivity ratios for the copolymerisation of monomers 1 and 2 would be given by the equations

$$r_{12} = (Q_1/Q_2) \exp[-e_1(e_1-e_2)]; \quad r_{21} = (Q_2/Q_1) \exp[-e_2(e_2-e_1)]$$

or $$\ln r_{12} = \ln (Q_1/Q_2) - e_1(e_1-e_2); \quad \ln r_{21} = \ln (Q_2/Q_1) - e_2(e_2-e_1)$$

Unfortunately, it was necessary to assign entirely arbitrary values for Q and e to one of the monomers; styrene was chosen, and the assigned values were $Q = 1.0$ and $e = -0.8$. It does not seem to have been thought strange that the hydrocarbon, styrene, should carry an electric charge equivalent to 80 % of that borne by an electron.

The Shortcomings of the *Q-e* Scheme

The originators of the *Q-e* Scheme were well aware of its imperfections, as is demonstrated by the following quotation from their 1947 paper[14]. "The most that can be claimed is that, to a reasonable approximation, the *Q-e* Scheme permits the codification of copolymerisation results in terms of the Q and e values of the various monomers. Further, the scheme is an empirical method of analysis, the parameters of which are susceptible only to a quasi-theoretical interpretation. It is not a solidly established 'theoretical' equation, in the usually accepted sense of that term. With these reservations, and in full recognition of the fact that a more satisfactory analysis of this problem may be developed in the future, it is the conclusion (of the authors) that the *Q-e* scheme is of decided utility and is in good harmony with experimental data."

There are four obvious serious objections, in principle, to the basis of 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;

(*iii*) dependence of rate constants on the relative permittivity of the medium [expected on the basis of assumption (*i*)] has not been observed, and

(*iv*) the arbitrary nature of the assignment of the parameters for styrene.

The Patterns of Reactivity Scheme ("Patterns")

This approach was based upon (*a*) rejection of the need to equate polarities of conjugate monomers and radicals (*e.g.*, M_1 and X_1), and (*b*) on the use of *exclusively experimentally-determined* parameters in place of Q and e, without the necessity of any arbitrary assignment.

The first step was to choose an experimental measure of the "general" reactivity of a radical, *i.e.*, its reactivity in a situation in which polarity may be presumed not to play a role; for this purpose, copolymerisation with styrene was chosen, and the relevant reactivity ratio for this process was written, in logarithmic form, as $\log r_{1S}$. It is implicitly assumed that both styrene monomer and the polymer radical derived from it are unresponsive to polar influences.

If a certain substrate (D, say) was chosen, and the reactivities ($\log r_{1D}$) of a series of radicals from the Basic Monomer Set compared graphically with the corresponding values for the parallel reaction with styrene ($\log r_{1S}$), it was found that the result was a linear plot; if, however, another substrate than styrene was selected as the reference compound, a pattern of points, rather than a straight line resulted. (It was the appearance and utility of this pattern of points that caused the resulting method for the analysis of reactivity to become known as the "Patterns of Reactivity Scheme" or, more succinctly, "Patterns".)

If the new reference compound was relatively non-polar, the departure from the straight line was small but, the more polar the compound, the larger the discrepancy between the pattern and a straight line. Evidently, this discrepancy was a measure of the polarity of the radical derived from species 1 and that of the reference compound, and it was thus necessary to quantify the radical's polar character. Since copolymerisation with styrene can reasonably be regarded as a non-polar reaction, a measure of the polarity of a radical may be obtained by comparison of its reactivity towards styrene and towards a highly polar monomer, *e.g.*, acrylonitrile (denoted by subscript A), *i.e* . $\log r_{1S} - \log r_{1A}$. Thus, both of the polar and non-polar parameters of radical reactivity are, in principle, available from experiment.

It is interesting to note that the electron density on the carbon atom bearing the unpaired electron in a polymer radical, as measured by the chemical shift in the NMR spectrum, correlates well with the polarity parameter proposed here[15].

The least amount of basic data that would permit the use of the scheme would be the monomer reactivity ratios for reaction of the monomers of interest with only acrylonitrile and styrene; it then becomes possible to develop an exceptionally simple and rapid method for the prediction of reactivity ratios through the following equations[4].

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

$\log r_{21} = \log(r_{2S}.r_{S1}) - [\log(r_{AS}.r_{S1}/r_{A1})][\log(r_{SA}.r_{2S}/r_{2A})]/\log(r_{AS}.r_{SA})$

All the parameters relating to a single participating species have been eliminated from the equations; the value of r_{12} depends, apart from the well-known r_{AS} and r_{SA}, only on four monomer reactivity ratios, each relating to the reaction of *either* monomer 1 *or* monomer 2 with *either* styrene *or* acrylonitrile. The same is true, *mutatis mutandis*, for r_{21}.

At first sight these equations may appear to be rather formidable but inspection reveals that they are extremely easy to use: they contain only reactivity ratios, two of which (r_{AS} and r_{SA}) are common to all systems while the remainder pertain to the separate copolymerisations of monomers 1 and 2 with styrene and acrylonitrile.

If the explicit values of r_{SA} (= 0.38) and r_{AS} (= 0.04) are inserted into this equation, it transforms into

$\log r_{12} = \log(r_{1S}.r_{S2}) + 0.55[\log(0.04r_{S2}/r_{A2})][\log(0.38r_{1S}/r_{1A})]$

As an example of the power of this method, these equation have been applied to the copolymerisation of 2-chloro(butadiene) and 2-vinylpyridine, the resulting values of the monomer reactivity ratios being r_{12} = 4.71 and r_{21} = 0.04, which may usefully be compared with the experimental values (5.19 and 0.06) and the predictions of the *Q-e* scheme (1.07 and 0.07).

Any other monomer, X say, can be used in place of acrylonitrile as the highly polar monomer of reference, in which case A has to be replaced everywhere by X, as in the following equation[4].

$\log r_{12} = \log(r_{1S}.r_{S2}) - [\log(r_{XS}.r_{S2}/r_{X2})][\log(r_{SX}.r_{1S}/r_{1X})]/\log[(r_{XS})(r_{SX})]$

As only a minority of monomers have reported reactivity ratios with acrylonitrile, this device greatly extends the range of monomers to which the Patterns Scheme may be applied; in fact the best monomer for this purpose is probably methyl methacrylate, for which a very substantial amount of data is available and which seems to lead to the most accurate predictions.

Comparison of Calculated and Experimental Values of Monomer Reactivity Ratios

It is not an easy matter to make a meaningful quantitative comparison of the experimental values of monomer reactivity ratios, r_{exp}, with those calculated, r_{calc}, either from the Patterns schemes or the *Q-e* scheme. For present purposes, the index chosen is the percentage discrepancy, pd, defined as

$$pd = 100[r_{exp} - r_{calc}]/r_{exp}$$

Scrutiny of Greenley's listing for data for monomers which have been studied in binary copolymerisation with acrylonitrile and styrene, and at least one other monomer from methyl methacrylate, methyl acrylate and methacrylonitrile (the remaining members of the Basic Monomer Set), produces a total of almost one hundred and fifty monomer pairs (or almost three hundred monomer reactivity ratios) for which the desired comparison can be made between experiment, on the one hand, and calculation by the Patterns scheme or the *Q-e* scheme, on the other. The resulting mean pd values are 68 for Patterns and 291 for *Q-e* (ref.[16]).

Without attaching overmuch significance to the actual mean pd values, it seems safe to conclude that the predictions of either form of the Patterns scheme are much more in line with the experimental data than are those of the *Q-e* scheme and, moreover, all the fundamental deficiences of the latter scheme are avoided.

Application of the Patterns Scheme to Transfer Reactions

By following parallel logic to the case of copolymerisation, it can be shown[4] that one would expect the value of a transfer constant to be predicted by the equation

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

Unlike its copolymerisation counterparts, this equation *does* contain a polarity parameter (π_1) relating to a single participant but this can be shown to be related to polymerisation data by the equation

$$\pi_1 = 0.385\log(r_{1A}/0.377r_{1S})$$

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 show that the mean discrepancy 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]} is 79 %.

Summary of Results for Transfer Reactions

The scheme estimates transfer constants to much better than an order of magnitude, indeed the mean discrepancies reported above are remarkably low even though the values of the transfer constants involved are spread over a range of no less than *nine orders of magnitude*, from 1.2×10^{-5} for styrene and toluene to 10 300 for styrene and copper (II) chloride; a modest discrepancy appears to be rather unobjectionable against this background.

The Termination Process

In principle, it would be interesting to understand the chemistry of the interaction of the two radicals involved in the termination reaction which ultimately brings the life of the radicals to an end. Determinations of the rate constants for typical termination put them in the region of 10^8 l $mol^{-1}s^{-1}$, comparable with the value expected if the rate of termination were controlled not by any chemical factors but simply by the rate of the diffusion process which brings the radicals close enough to interact with almost zero activation energy[16]. Chemical interpretation of the termination process is of little or no significance.

Conclusion

After a very long period during which only semi-quantitative predictions of reactivity could be made, and on a far from satisfactory theoretical basis, it has become possible, through the Patterns Scheme, to deduce useful values of reactivity ratios and transfer constants entirely from a knowledge of experimentally-determined parameters. Unjustified assumptions in the early studies have been eliminated, so that the only limitation resides in the accuracy of the determination of the reactivity ratios reported in the polymer chemistry literature.

REFERENCES

1. Matyjaszewski K., Patten T. E., Xia J.: J. Am. Chem. Soc. *119*, 674 (1997).
2. Price C. C.: J. Polym. Sci. *1*, 83 (1946).
3 . Bamford C. H., Jenkins A. D., Johnston R.: Trans. Farad. Soc. *55*, 418 (1959).
4. Jenkins A. D.: J. Polym. Sci. Part A Polym. Chem. *34*, 3495 (1996).
5. Briers F., Chapman D. L., Walters E.: J. Chem. Soc. *1926*, 562.
6. O'Driscoll K. F., Mahabadi H.: J. Polym. Sci. *14*, 869 (1976).
7. Olaj O. F., Bitai I., Gleixner G.: Makromol. Chem. *186*, 2580 (1985).
8. Mayo F. R., Lewis F. M.: J. Am. Chem. Soc. *66*, 1594 (1944).
9. Wall F. T.: J. Am. Chem. Soc. *66*, 2050 (1944).
10. Alfrey T., Goldfinger G.: J. Chem. Phys. *12*, 205 (1944).
11. Greenley R. Z.: *Polymer Handbook*, 4th Edition, p.II/181. Wiley, New York 1999.
12. Alfrey T., Merz E., Mark H.: J. Polym. Sci. *1*, 37 (1946).
13. Lewis F. M., Mayo F. R., Hulse W. F.: J. Am. Chem. Soc. *67*, 1701 (1945).
14. Alfrey T., Price C. C.: J. Polym. Sci. *2*, 101 (1947).
15. Jenkins A. D., Hatada K., Kitayama T., Nishiura T.: J. Polym. Sci. *38*, 4336 (2000).
16. Jenkins A. D., Jenkins J.: Macromol. Symp. *111*, 159 (1996).

A. Jenkins *(University of Sussex, Brighton, Sussex, U.K.):* **Reactivity in Conventional Radical Polymerisation**

The best-known procedure for predicting monomer reactivity ratios in binary radical polymerisation is the so-called *Q-e* Scheme, which was advanced over 50 years ago. This had an unsound theoretical basis and provided results of low accuracy. The present paper describes the application of the Patterns of Reactivity Scheme, which draws exclusively on experimental data (reactivity ratios) for its raw material, and which provides far more satisfactory results.