First derivation of an intrinsic Q-e scheme to predict monomer reactivity ratios for radical copolymerization and first calculation of Q-e values for polymer radicals

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1. Introduction

The Q-e scheme [1], proposed by Alfrey and Price in 1947, is a mathematical model that expresses the monomer reactivity ratio of radical copolymerization of vinyl monomers in terms of two parameters. The Q-e scheme continues to be important not only for engineering practicality but also from the fundamentals of polymer chemistry, because if the Q-e values of monomers are known, the reactivity ratios can be predicted quantitatively for unknown monomer pairs. However, several shortcomings of the Q-e scheme have been pointed out since its proposal, and they have remained unresolved for a long time. Recently, we have derived an intrinsic Q-e scheme to improve the Q-e scheme [2]. This scheme eliminates the shortcomings of the Q-e scheme and provides a more accurate prediction of reactivity ratios. Furthermore, the Q-e values of polymer radicals were successfully determined separately from those of monomers for the first time. The intrinsic Q-e scheme is described below.

2. Monomer reactivity ratio and Q-e scheme based on the terminal model

The simplest model to represent radical copolymerization is the terminal model, in which the nature of the growing radical is determined solely by the monomer units comprising the terminal radical; copolymerization between two monomers M1 and M2 is represented by four growing reactions in the terminal model, as shown in Figure 1.
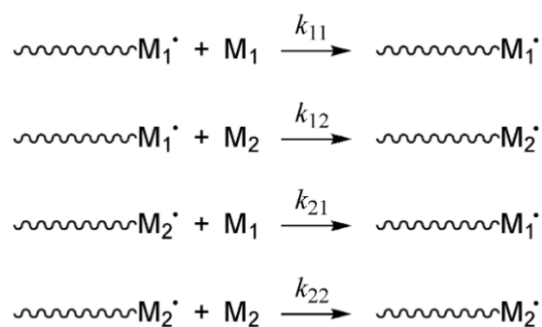

図1. 末端モデルによる共重合生長反応

F 1. Copolymerization growth reaction by terminal model

where k is the rate constant for each growth reaction. The monomer reactivity ratio (r) of

the radical copolymerization of monomers M1 and M2 is defined as the ratio of the rate constants as follows

$$r_1 \equiv r_{12} = \frac{k_{11}}{k_{12}} \#(1)$$

$$r_2 \equiv r_{21} = \frac{k_{22}}{k_{21}} \#(2)$$

Therefore, the larger the value of reactivity ratio, the more easily the growing end radicals react with homogeneous monomers, and the smaller the value, the more easily they react with heterogeneous monomers. The prediction of the reactivity ratio is important because if the monomer reactivity ratio is known, it is possible to predict the monomer composition and chain distribution of the polymer chain generated in case of copolymerization at a certain monomer stocking ratio. The Q-e scheme has long been used for this purpose.

In their induction of the Q-e scheme, Alfrey and Price assumed that the activation energy term of the rate constant (k12) for the biogenesis reaction between radical 1 and monomer 2 can be partitioned as follows [1].

$$k_{12} = A_{12} exp\left[-\left(p_1 + q_2 + e_1 e_2\right)\right] \#(3)$$

Here, A12 is the frequency factor, p1 is the activation factor for the general reactivity of radical 1, q2 is the activation factor for the general reactivity of monomer 2, and e1 and e2 are the respective electrical factors. They considered A12 to be essentially constant and rewrote equation (3) as follows:

$$k_{12} = P_{R(1)} Q_{M(2)} exp\left(- e_{R(1)} e_{M(2)}\right) \#(4)$$

Here, PR(1) represents the characteristic amount of radical 1, QM(2) represents the average reactivity of monomer 2, eR(1) is the amount proportional to the charge of the terminal group of radical 1, and eM(2) is the amount proportional to the charge of the double bond of monomer 2. To clearly distinguish the Q-e parameters for monomers and polymer radicals, from now on the subscripts M and R denote monomers and polymer radicals, respectively, and the number in parentheses denotes the monomer species. If this relationship is also applied to k11, k21, and k22 to express the reactivity ratios, the constant P cancels out and the Q-e scheme is obtained as in the following equation.

$$r_{12} = \left(\frac{Q_{M(1)}}{Q_{M(2)}}\right) exp\left[- e_{R(1)}\left(e_{M(1)} - e_{M(2)}\right)\right] \#(5)$$

$$r_{21} = \left(\frac{Q_{M(2)}}{Q_{M(1)}}\right) exp\left[- e_{R(2)}\left(e_{M(2)} - e_{M(1)}\right)\right] \#(6)$$

Let us introduce an important point made by Imoto [3] regarding the Q-e scheme. According to Imoto, equation (4) is not valid in case of single polymerization of k11 or k22. The reason for this is that k11 and k22 should be inversely proportional to the Q value, since k11 and k22 generally decrease as the monomer resonance effect (i.e., Q value) increases.

Imoto further writes In any case, the Q-e scheme has been widely used for a long time and is certainly wrong in principle. Nevertheless, the scheme is useful and widely used. We sincerely hope that further in-depth study will be forthcoming." Our study of the intrinsic scheme is an attempt to answer this.

3. how to obtain Q-e values

To obtain Q-e values using the Q-e scheme, Young's method is generally used; in Young's method, the Q parameter is first eliminated by expressing the product of reactivity ratios r12r21 in equations (5) and (6). Furthermore, assuming eR=eM, the following equation is obtained.

$$r_{12}r_{21} = exp\left[-\left(e_{M(2)} - e_{M(1)}\right)^2\right] \#(7)$$

Here, if styrene (S) is used as the reference monomer for monomer 1, the e-value of the target monomer 2 can be expressed by the following equation.

$$e_{M(2)} = e_S \pm \sqrt{-ln\left(r_{S2}r_{2S}\right)} \#(8)$$

The Q value can be obtained by substituting the obtained eM(2) into the following equation, which is a variant of equation (5).

$$Q_{M(2)} = \left(\frac{Q_S}{r_{S2}}\right)exp\left[-e_S\left(e_S - e_{M(2)}\right)\right] \#(9)$$

For the Q-e value of the reference styrene, QS = 1.0 and eS = -0.8 are adopted according to Alfrey-Price. The Q-e values of many monomers have been determined by Young's method and are summarized in the second edition of the Polymer Handbook [4]. It is the arbitrariness of the choice. In practice, a positive sign is employed for normal monomers and a negative sign for monomers that are considered chemically more donor-like than styrene. There is also the arbitrariness of modifying the values appropriately, since the square root in the tabular expression of the e-value is imaginary in cases where r12r21>1 or r12r21=0. Greenley's method attempts to avoid these arbitrariness. In this method, six major monomers (acrylic acid, acrylonitrile, butadiene, methyl acrylate, methacrylonitrile, and methyl methacrylate) with relatively narrow experimental distributions of reactivity ratios are added as reference monomers To obtain Q-e values, the following formula, a variant of equation (3), is used.

$$\left[ln\,ln\left(\frac{Q_{M(1)}}{r_{12}}\right) - e_{M(1)}^2\right] = -e_{M(2)}e_{M(1)} + ln\,ln\,Q_{M(2)} \#(10)$$

Using the Q-e values of each reference monomer 1 obtained by Young's method, plot ln

QM(1)r12 -eM(1)2 on the left-hand side against eM(1), and obtain eM(2) and ln QM(2) for monomer 2 from the slope and intercept, respectively. In this way, Q-e values for monomers other than the reference monomer can be obtained without any arbitrariness; Greenley's Q-e values for monomers are summarized in the fourth edition of the Polymer Handbook [5]. It should be noted that Greenley's method uses only equation (3) for the reactivity ratio and does not reflect the contribution of equation (4) [6].

Using the Q-e scheme is simpler because the reactivity ratio can be expressed in terms of just two parameters. In addition, since it is recognized from previous experimental and quantum chemical calculation studies that the Q value represents general reactivity (resonance effect) and the e value represents polarity effect, the Q-e value is useful not only for radical polymerization but also for determining the cationic or anionic polymerizability of a monomer. However, the problem of arbitrariness in determining the Q-e value, as mentioned earlier, remains inherently problematic.

4. Derivation of generalized Q-e scheme

Our objective was to eliminate arbitrariness in obtaining e-values, and for this purpose, we considered constructing a scheme using two reference monomers in the Q-e scheme. However, after much trial and error, we came to the realization that instead of using the Q-e scheme as it is, we need to modify the Q-e scheme to include the Q values of the radicals in the tabular expression of the reactivity ratio. In deriving the modified Q-e scheme, we considered dividing the activation free energy difference corresponding to the reactivity ratio r12 into each contribution, rather than dividing the activation term of the rate constant into each contribution as in the Q-e scheme. The derivation is shown below.

Based on transition state theory, the reactivity ratio can be expressed as follows.

$$r_{12} = \frac{k_{11}}{k_{12}} = exp\left[-\frac{\left(\Delta G^{\ddagger}_{R(1)M(1)} - \Delta G^{\ddagger}_{R(1)M(2)}\right)}{RT}\right] \#(11)$$

Here, $\Delta G_{R(1)M(1)}$ and $\Delta G_{R(1)M(2)}$ are the activation free energies of k11 and k12, respectively. We consider that the free energy difference in RT units can be partitioned by radical-specific values ($q_{R(1)}$), monomer-specific values ($q_{M(2)}$), and intersection terms between radical 1 and monomer 1, and radical 1 and monomer 2 ($e_{R(1)M(1)}$ and $e_{R(1)M(2)}$, respectively), as in the following equation:

$$-\frac{\left(\Delta G^{\ddagger}_{R(1)M(1)} - \Delta G^{\ddagger}_{R(1)M(2)}\right)}{RT} \cong -\left(q_{R(1)} - q_{M(2)}\right) - \left(e_{R(1)M(1)} - e_{R(1)M(2)}\right) \#(12)$$

Then, the following parameters are introduced.

$$Q_{R(1)} = exp\left(-q_{R(1)}\right) \#(13)$$
$$Q_{M(2)} = exp\left(-q_{M(2)}\right) \#(14)$$

Furthermore, assume that the cross term can be approximated by a product of e-values as follows:

$$e_{R(1)M(1)} - e_{R(1)M(2)} \cong e_{R(1)}\left(e_{M(1)} - e_{M(2)}\right) \#(15)$$

From these, the following equation is obtained:

$$r_{12} = \left(\frac{Q_{R(1)}}{Q_{M(2)}}\right)exp\left[- e_{R(1)}\left(e_{M(1)} - e_{M(2)}\right)\right] \#(16)$$

Similarly, for r21, the following equation is obtained:

$$r_{21} = \left(\frac{Q_{R(2)}}{Q_{M(1)}}\right)exp\left[- e_{R(2)}\left(e_{M(2)} - e_{M(1)}\right)\right] \#(17)$$

These differ from Alfrey-Price's original Q-e scheme in that they include the Q values of the radicals, which we will refer to as the generalized Q-e scheme. In equations (16) and (17), the generalized Q-e scheme coincides with the original Q-e scheme in case QR(1)=QM(1) and QR(2)=QM(2). Therefore, we can say that the Alfrey-Price Q-e scheme is encapsulated in the generalized Q-e scheme. If the ratio of rate constants (i.e., the activation free energy difference) can be partitioned and expressed in terms of the contribution of each term, as has been pointed out for the Q-e scheme, the radical copolymerization reaction may follow a linear free energy relationship [7], similar to the Hammett rule and others.

5. Derivation of the intrinsic Q-e scheme
The intrinsic Q-e scheme is then derived by applying the two reference monomers to the generalized Q-e scheme. The monomer reactivity ratio between monomer 1 and the reference monomers styrene (S) and acrylonitrile (A) is expressed by the following six equations from equations (16) and (17).

$$r_{1S} = \left(\frac{Q_{R(1)}}{Q_{M(S)}}\right)exp\left(- e_{R(1)}\delta_{M(1)}\right) \#(18)$$

$$r_{S1} = \left(\frac{Q_{R(S)}}{Q_{M(1)}}\right)exp\left(e_{R(S)}\delta_{M(1)}\right) \#(19)$$

$$r_{1A} = \left(\frac{Q_{R(1)}}{Q_{M(A)}}\right)exp\left[- e_{R(1)}\left(\delta_{M(1)} - \delta_{M(A)}\right)\right] \#(20)$$

$$r_{A1} = \left(\frac{Q_{R(A)}}{Q_{M(1)}}\right)exp\left[e_{R(A)}\left(\delta_{M(1)} - \delta_{M(A)}\right)\right] \#(21)$$

$$r_{SA} = \left(\frac{Q_{R(S)}}{Q_{M(A)}}\right)exp\left(e_{R(S)}\delta_{M(A)}\right) \#(22)$$

$$r_{AS} = \left(\frac{Q_{R(A)}}{Q_{M(S)}}\right)exp\left(- e_{R(A)}\delta_{M(A)}\right) \#(23)$$

Here, we introduced M(1) and R(1), representing the e-values relative to styrene for monomer 1 and radical 1, respectively, as follows:

$$\delta_{M(1)} = e_{M(1)} - e_{M(S)} \#(24)$$

$$\delta_{R(1)} = e_{R(1)} - e_{R(S)} \#(25)$$

We assume that the Q values of the styrene monomer and radical are constant (QS) and equal.

$$Q_{M(S)} = Q_{R(S)} = Q_S \#(26)$$

This allows us to eliminate the Q-value terms from three of the six equations (equations (18), (20), and (22) and (19), (21), and (23), respectively), and to express. $\delta_{M(1)}$ and

$$\delta_{R(1)}$$

as follows:

$$\delta_{M(1)} = \frac{\ln\ln\left(\frac{r_{A1}}{r_{S1}r_{AS}}\right)}{\delta_{R(A)}} = \frac{e^{\circ}_{M(1)}}{\delta_{R(A)}} \#(27)$$

$$\delta_{R(1)} = \frac{\ln\ln\left(\frac{r_{1A}}{r_{1S}r_{SA}}\right)}{\delta_{M(A)}} = \frac{e^{\circ}_{R(1)}}{\delta_{M(A)}} \#(28)$$

The following parameters are defined here.

$$e^{\circ}_{M(1)} = \ln\ln\left(\frac{r_{A1}}{r_{S1}r_{AS}}\right) \#(29)$$

$$e^{\circ}_{R(1)} = \ln\ln\left(\frac{r_{1A}}{r_{1S}r_{SA}}\right) \#(30)$$

From the relationship between equations (24) and (25) and (27) and (28), the e-values of the monomer and polymer radicals can be expressed as follows:

$$e_{M(1)} = e_{M(S)} + \left(\frac{e^{\circ}_{M(1)}}{\delta_{R(A)}}\right) \#(31)$$

$$e_{R(1)} = e_{R(S)} + \left(\frac{e^{\circ}_{R(1)}}{\delta_{M(A)}}\right) \#(32)$$

The Q values of the monomer and polymer radicals can be expressed by rewriting equations (18) and (19) as follows:

$$Q_{M(1)} = \left(\frac{Q_S}{r_{S(1)}}\right) exp\left(e_{R(S)}\delta_{M(1)}\right) = Q_S Q^{\circ}_{M(1)} exp\left(e_{R(S)}\delta_{M(1)}\right) \#(33)$$

$$Q_{R(1)} = r_{1S}Q_S exp\left(e_{R(1)}\delta_{M(1)}\right) = Q_S Q^{\circ}_{M(1)} exp\left(e_{R(S)}\delta_{M(1)}\right) \#(34)$$

The following parameters are defined here:

$$Q^{\circ}_{M(1)} = \frac{1}{r_{S1}} \#(35)$$

$$Q^{\circ}_{R(1)} = r_{1S} \#(36)$$

Substituting equations (31) and (32) into equation (16) of the generalized Q-e scheme, the

reactivity ratio r12 can be expressed as follows：

$$r_{12} = \left(\frac{Q_{R(1)}}{Q_{M(2)}}\right)exp\left[-e_{R(1)}\left(e_{M(1)} - e_{M(2)}\right)\right] = \left(\frac{Q_{R(1)}}{Q_{M(2)}}\right)exp\left[-e_{R(1)}\left(\delta_{M(1)} - \delta_{M(2)}\right)\right] = \left(\frac{Q^{\circ}_{R(1)}}{Q_{M(2)}}\right)exp\left(e_{R(1)}\delta_{M(1)} - e_{R(S)}\delta_{M(2)}\right)$$

We assume that the Q values of the acrylonitrile monomer and polymer radicals are constant (QA) and equal, as is the case for styrene assumed in equation (26).

$$Q_{M(A)} = Q_{R(A)} = Q_A \#(38)$$

From the assumption of Q values for acrylonitrile and styrene, the product of equations (22) and (23) can be easily expressed as follows：

$$r_{AS}r_{SA} = exp\left(-\delta_{R(A)}\delta_{M(A)}\right)\#(39)$$

Using this relationship, equation (37) can be further expressed as follows:

$$r_{12} = \left(\frac{Q^{\circ}_{R(1)}}{Q^{\circ}_{M(2)}}\right)exp\left[-\frac{e^{\circ}_{R(1)}e^{\circ}_{M(2)}}{\ln\ln\left(r_{AS}r_{SA}\right)}\right]\#(40)$$

The reactivity ratio r21 can be similarly expressed as follows:

$$r_{21} = \left(\frac{Q^{\circ}_{R(2)}}{Q^{\circ}_{M(1)}}\right)exp\left[-\frac{e^{\circ}_{R(2)}e^{\circ}_{M(1)}}{\ln\ln\left(r_{AS}r_{SA}\right)}\right]\#(41)$$

Equations (40) and (41) are called the intrinsic Q-e scheme, and $QR(1)^{\circ}$, $QM(1)^{\circ}$, $eR(1)^{\circ}$, and $eM(1)^{\circ}$ are called the intrinsic Q-e parameters. Substituting the intrinsic Q-e parameters into the intrinsic Q-e scheme yields the following equation:

$$r_{12} = r_{1S}r_{S2}exp\left[-\frac{\ln\ln\left(\frac{r_{1A}}{r_{1S}r_{SA}}\right)\ln\ln\left(\frac{r_{A2}}{r_{S2}r_{AS}}\right)}{\ln\ln\left(r_{AS}r_{SA}\right)}\right]\#(42)$$

$$r_{21} = r_{2S}r_{S1}exp\left[-\frac{\ln\ln\left(\frac{r_{2A}}{r_{2S}r_{SA}}\right)\ln\ln\left(\frac{r_{A1}}{r_{S1}r_{AS}}\right)}{\ln\ln\left(r_{AS}r_{SA}\right)}\right]\#(43)$$

Therefore, using the intrinsic Q-e scheme, the reactivity ratio between monomers 1 and 2 can be calculated if the reactivity ratios of monomers 1 and 2 to the reference monomers S and A are known. Since the only assumptions used to derive the intrinsic Q-e scheme are equations (26) and (38), there is absolutely no arbitrariness in the calculation of reactivity ratios by the intrinsic Q-e scheme.

Here, the tabular expression [8] of Jenkins' revised patterns A and S scheme, which had been developed separately from the Q-e scheme, is shown below:

$$\log\log r_{12} = \log\log\left(r_{1S}r_{S2}\right) - \frac{\log\log\left(\frac{r_{AS}r_{S2}}{r_{A2}}\right)\log\log\left(\frac{r_{SA}r_{1S}}{r_{1A}}\right)}{\log\log\left(r_{AS}r_{SA}\right)}\#(44)$$

$$\log\log r_{21} = \log\log\left(r_{2S}r_{S1}\right) - \frac{\log\log\left(\frac{r_{AS}r_{S1}}{r_{A1}}\right)\log\log\left(\frac{r_{SA}r_{2S}}{r_{2A}}\right)}{\log\log\left(r_{AS}r_{SA}\right)}\#(45)$$

The Patterns scheme was derived from the idea of using chain transfer reactions to measure the reactivity of polymer radicals, which is quite different in conception from the Q-e scheme. Therefore, it is surprising and unexpected for us that the final reactivity ratio equations agree as they do. A series of revised patterns schemes have been shown to be more accurate in predicting reactivity ratios than the Q-e scheme, but unfortunately they have not been used as much as the Q-e scheme. The study of the intrinsic Q-e scheme may lead to a review of Jenkins' work in terms of the Q-e scheme.

6. accuracy of prediction of monomer reactivity ratios by the intrinsic Q-e scheme

In this section, we present some examples of predictions of reactivity ratios by the intrinsic Q-e scheme: examples of common monomer combinations that are relatively well predicted by Alfrey-Price's Q-e scheme are shown in Table 1, and examples of special monomer combinations that are difficult to predict by the Q-e scheme are shown in Table 2. For the monomer pair reactivity ratios shown in Table 1, the predictions by the original Q-e scheme reproduce the experimental values well. The same is true for the intrinsic Q-e scheme, but the error from the experimental values is smaller than that of the original Q-e scheme. On the other hand, for the monomer pairs shown in Table 2, the predictions by the original Q-e scheme are inferior to the experimental values with large errors, while the predictions by the intrinsic Q-e scheme correspond well to the experimental values with small errors. Thus, the intrinsic Q-e scheme predicts the monomer reactivity ratio more accurately than the original Q-e scheme.

表1．一般的モノマー対の反応性比のQ-eスキームと固有Q-eスキームによる予測値

モノマー対 1/2		実験値	Q-e[a]	固有Q-e
MMA/MA	r_{12}	2.15	1.91	2.22
	r_{21}	0.40	0.49	0.29
MMA/MAN	r_{12}	0.75	1.01	0.88
	r_{21}	0.50	0.91	0.54
MA/MAN	r_{12}	0.50	0.54	0.51
	r_{21}	2.00	1.86	2.69
平均絶対誤差			0.20	0.18

[a]GreenleyのQ-e値を用いた。

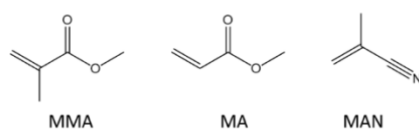Table 1. Predictions by Q-e scheme and intrinsic Q-e scheme of reactivity ratios for generic monomer pairs

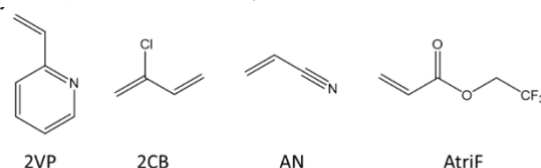

MMA MA MAN

表２．特殊なモノマー対の反応性比のQ-eスキームと固有Q-eスキームによる予測値

モノマー対 1/2		実験値	Q-e[a]	固有Q-e
2VP/2CB	r_{12}	5.19	1.07	4.71
	r_{21}	0.06	0.07	0.04
AN/AtriF	r_{12}	1.25	0.54	1.03
	r_{21}	0.93	1.71	0.78
平均絶対誤差			1.41	0.22

[a]GreenleyのQ-e値を用いた。

Table 2. Predictions by Q-e scheme and intrinsic Q-e scheme of reactivity ratios for special monomer pairs

2VP   2CB   AN   AtriF

7. Calculation of Q-e values for polymer radicals and monomers

In this section, the Q-e values of polymer radicals and monomers are determined separately using the intrinsic Q-e scheme. Equations (31)-(34) can be used for this purpose. Alfrey-Price's value (QS=1, eM(S)=eR(S)=-0.8) is used for the Q-e value of styrene, Greenley's value (eM(A)=eR(A)=1.23) for the Q-e value of acrylonitrile, rAS=0.04 and rSA=0.04 as the reactivity ratio between styrene and acrylonitrile. 04 and rSA=0.38 as the reactivity ratio between styrene and acrylonitrile, equations (31)-(34) can be expressed as follows:

$$e_{M(1)} = -0.8 + \frac{1}{2.03}\ln\ln\frac{r_{A1}}{0.04 r_{S1}} \#(46)$$

$$e_{R(1)} = -0.8 + \frac{1}{2.03}\ln\ln\frac{r_{1A}}{0.38 r_{1S}} \#(47)$$

$$Q_{M(1)} = \frac{1}{r_{S1}}\exp\left[\frac{-0.8\ln\ln\left(\frac{r_{A1}}{0.04 r_{S1}}\right)}{2.03}\right] \#(48)$$

$$Q_{R(1)} = r_{1S}\exp\left\{\left[-0.8 + \frac{\ln\ln\left(\frac{r_{1A}}{0.38 r_{1S}}\right)}{2.03}\right]\left[\frac{\ln\ln\left(\frac{r_{A1}}{0.04 r_{S1}}\right)}{2.03}\right]\right\} \#(49)$$

The Q-e values of monomer and polymer radicals calculated for several monomers are shown in Table 3. We are the first to successfully determine the Q-e values of polymer radicals and monomers separately. Although the Q-values between monomers and polymer radicals are relatively similar, there are monomer and polymer radical e-values that have different signs as well as numerical values. Thus, it can be seen that in the original Q-e scheme, the assumption adopted in obtaining the Q-e values (eR=eM) is not necessarily valid. For example, in the 2CB discussed in the example of special monomer pairs in Table 2, the e-values of the monomer and polymer radicals have different signs and the e-value of the polymer radical is negative. This suggests that the polymer radical is more donor than the monomer, which is consistent with the fact that 2CB as a polymer radical is considered donor because it forms allyl radicals (i.e., because the allyl cation that has released an electron is more stable). Interestingly, Greenlery's Q-e values were found to correspond to the Q-e values of the monomers determined here (see Ref. 2 for details). Thus, care must be taken as to which e-value to use, since Young's e-value indicates the average properties of the monomer and polymer radicals, whereas Greenley's e-value indicates only the properties of the monomer.

表３．算出したモノマーとポリマーラジカルのQ-e値

モノマー	Q_M	Q_R	e_M	e_R
スチレン (S): 基準	1	1	−0.8	−0.8
アクリロニトリル (A): 基準	0.51	0.54	1.26	1.26
ブタジエン (B)	1.20	0.83	−0.32	−1.10
2-クロロブタジエン (2CB)	6.64	3.10	0.92	−0.47
イソプレン (I)	1.80	1.44	−0.56	−1.02
無水マレイン酸 (MAh)	0.26	0.04	2.17	0.42
メタクリル酸 (MAc)	2.37	0.30	−0.10	−0.80
メタクリロニトリル (MAN)	0.70	0.72	0.85	0.48
アクリル酸メチル (MA)	0.29	0.42	1.10	0.44
メタクリル酸メチル (MMA)	0.93	0.55	0.15	0.20
酢酸ビニル (VA)	0.01	0.02	−0.35	0.13
塩化ビニル (VC)	0.03	0.04	−0.07	−0.42
ビニルエチルエーテル (VEE)	0.02	0.06	−1.67	−0.23
2-ビニルピリジン (2VP)	1.02	0.66	−0.04	−0.84
塩化ビニリデン (VDC)	0.24	0.14	0.28	0.21

Table 3. Calculated Q-e values of monomer and polymer radicals

8. Conclusion

In this paper, we have shown that the intrinsic Q-e scheme can be derived by using two reference monomers as opposed to the generalized Q-e scheme that extends Alfrey-Price's Q-e scheme to include the Q values of polymer radicals. The prediction accuracy of the monomer reactivity ratio of the intrinsic Q-e scheme is better than that of the Alfrey-Price Q-e scheme and can be used more generally. The Q-e values of monomer and polymer radicals can also be determined separately. With the intrinsic Q-e scheme, these Q-e values are no longer needed for predicting reactivity ratios at the earliest, but they may be utilized in the interpretation and design of monomers and polymer radicals. We are currently conducting a detailed study of the obtained Q-e values of monomers and polymer radicals by DFT calculations. We are also in the process of studying the pre-terminating group effect, which is important in radical copolymerization.

[Ref.]

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