



**Determining the Q-e values of polymer radicals and monomers separately through the derivation of an intrinsic Q-e scheme for radical copolymerization**

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## ARTICLE

## Determining the $Q$ - $e$ values of polymer radicals and monomers separately through the derivation of an intrinsic $Q$ - $e$ scheme for radical copolymerization<sup>A</sup>

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Herein, we describe the first non-arbitrary determination of the  $Q$ - $e$  values for individual polymer radicals and monomers. For this purpose, two reference monomers were subjected to a  $Q$ - $e$  scheme, which was extended by including the individual radical and monomer parameters to derive a novel scheme, namely the intrinsic  $Q$ - $e$  scheme. The derivation of this scheme was straightforward and was expressed only through the reactivity ratios among a target monomer and the reference monomers. The expression of the reactivity ratios by the scheme was found to be equivalent to that of the revised patterns A,S scheme, indicating the excellent predictability of the reactivity ratios. We then employed the intrinsic  $Q$ - $e$  parameters to successfully calculate the  $Q$ - $e$  values of individual radicals and monomers. A relatively good correlation was observed between the radical and monomer  $Q$  values ( $Q_R$  and  $Q_M$ , respectively), while no clear correlation was observed between the radical and monomer  $e$  values ( $e_R$  and  $e_M$ , respectively), as some of them significantly deviated from the condition  $e_R = e_M$  or had different signs. Therefore, the approximation of  $e_R = e_M$  in the original  $Q$ - $e$  scheme is not necessarily valid in some cases. Since the  $Q_M$ - $e_M$  values correlate well with Greenley's  $Q$ - $e$  values, they are both suitable as indicators of the monomer properties. Finally, application of the intrinsic  $Q$ - $e$  scheme to transfer constants for transfer agents is also described.

### Introduction

Herein, we introduce the  $Q$ - $e$  scheme and the relevant schemes, such as the revised patterns scheme, to derive a new scheme for radical polymerization, which is extended to handle individual radical and monomer  $Q$ - $e$  parameters. The  $Q$ - $e$  scheme proposed by Alfrey and Price<sup>1</sup> in 1947 has been used to quantitatively predict unknown reactivity ratios using the  $Q$ - $e$  parameters of individual monomers, which are independent of monomer pairs, and are determined from the experimental reactivity ratios. According to Alfrey and Price, the reactivity ratios between monomers 1 and 2 can be expressed as follows:

$$r_1 = r_{12} = k_{11}/k_{12} = (Q_{M(1)}/Q_{M(2)})\exp[-e_{R(1)}(e_{M(1)} - e_{M(2)})], \quad (1)$$

$$r_2 = r_{21} = k_{22}/k_{21} = (Q_{M(2)}/Q_{M(1)})\exp[-e_{R(2)}(e_{M(2)} - e_{M(1)})], \quad (2)$$

where the notations  $r_{12}$  and  $r_{21}$  instead of  $r_1$  and  $r_2$  are used for the mathematical expressions presented in this study, and to distinguish the  $Q$ - $e$  parameters accordingly, M and R represent the monomer and radical, respectively. The  $Q$ - $e$  value can be obtained by approximating the  $e$  value of a polymer

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radical to that of the conjugate monomer, i.e.,  $e_R = e_M$ , and by setting the  $Q$ - $e$  value for the reference monomer in advance. In general, styrene (S) is chosen as the reference monomer with  $Q_{M(S)} = 1$  and  $e_{M(S)} = -0.8$ ,<sup>2</sup> and the  $Q$ - $e$  value is obtained by applying the experimental reactivity ratio between the target monomer and styrene to Equations (1) and (2). There are several ways to determine the  $Q$ - $e$  values, and the accuracy of the reactivity ratio predicted by the  $Q$ - $e$  scheme not only depends on the reactivity ratios<sup>3</sup> used to calculate the  $Q$ - $e$  values, but also on the calculation method employed.<sup>4</sup> Previously, Young and Greenley reported the  $Q$ - $e$  values for various monomers in the *Polymer Handbook*.<sup>5,6</sup>

The method proposed by Young<sup>7</sup> has been commonly used because of its simplicity; however, there is an arbitrary choice of sign when determining the  $e$  value using the following equation derived from the product of Equations (1) and (2):

$$e_{M(2)} = e_{M(1)} \pm \sqrt{-\ln(r_{12}r_{21})}, \quad (3)$$

where the subscripts 1 and 2 represent styrene and the target monomer, respectively. A positive sign is selected for general monomers, and a negative sign is selected when the monomer is more donor-like than styrene. For  $r_{12}r_{21} > 1$ ,  $r_{12}r_{21}$  is set to  $< 1$ , since the square root is an imaginary number. Moreover, when  $r_{12}r_{21} = 0$ , the square root of which also gives an imaginary number, and  $r_{12}r_{21}$  is adjusted to a small value to provide a reasonable  $e$  value. The  $Q_{M(2)}$  value is obtained by substituting the experimental reactivity ratio,  $r_{12}$ , and the calculated  $e_{M(2)}$  into the following equation, which is a variation of Equation (1):

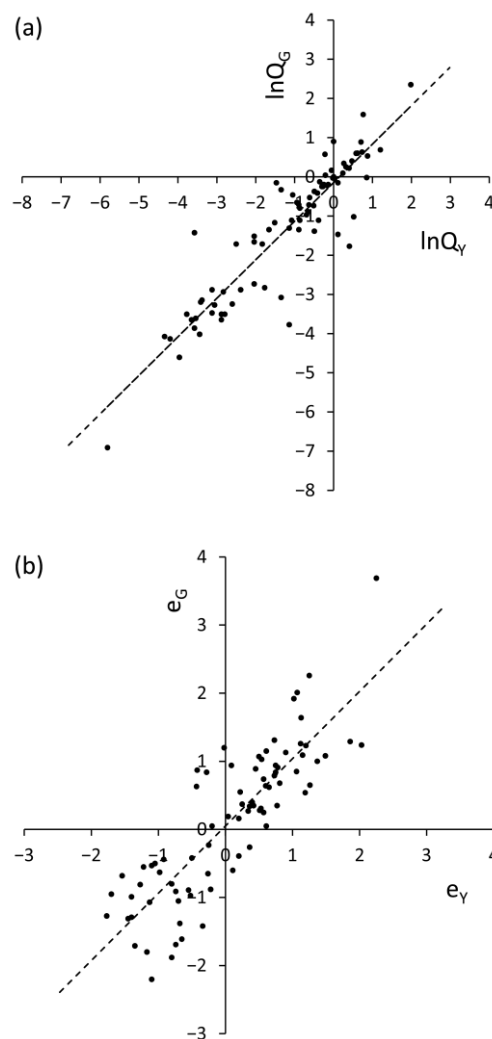
$$Q_{M(2)} = (Q_{M(1)}/r_{12}) \exp[-e_{M(1)}(e_{M(1)} - e_{M(2)})]. \quad (4)$$

On the other hand, to avoid such arbitrariness in the Young's method, Greenley<sup>6</sup> used six primary monomers with a relatively narrow distribution of the reported reactivity ratios, such as acrylic acid, acrylonitrile, butadiene, methyl acrylate, methacrylonitrile, and methyl methacrylate, as additional reference monomers. The  $Q$ - $e$  value of the target monomer can be obtained from Equation (5), which is derived from Equation (1), using the reactivity ratio between the target and reference monomers, and the  $Q$ - $e$  value of the reference monomer obtained by Young's method, as shown below:

$$[\ln(Q_{M(1)}/r_{12}) - e_{M(1)}^2] = -e_{M(2)}e_{M(1)} + \ln Q_{M(2)}, \quad (5)$$

where the subscripts 1 and 2 represent a reference monomer and the target monomer, respectively. The values on the left-hand side of the equation are plotted against  $e_{M(1)}$  to obtain  $-e_{M(2)}$  and  $\ln Q_{M(2)}$  from the slope and the intercept, respectively. Greenley's method removes the arbitrariness for all but the six primary monomers. Determination of the  $Q$ - $e$  value of the target monomer requires a reactivity ratio with preferably three or more reference monomers whose  $Q$ - $e$  values are known. In addition, unlike Young's method, Greenley used Equation (1) alone without any combination with Equation 2.<sup>4</sup> Figs. 1(a) and 1(b) compare the  $Q$ - $e$  values of 82 monomers

reported by Greenley<sup>6</sup> and Young.<sup>5</sup> For both methods, the corresponding  $Q$  and  $e$  values show correlations with  $r^2 = 0.835$  and  $r^2 = 0.715$ , respectively. The latter moderate correlation is attributed to different definitions of the  $e$  value in Greenley's and Young's methods, respectively, wherein Young's  $e$  value corresponds to the mean contributions of both the radical and the monomer because of the approximation,  $e_R = e_M$ . On the other hand, Greenley's  $e$  value corresponds only to the monomer contribution since only the reactivity ratio,  $r_{X2}$ , is employed, where  $X$  indicates a reference monomer and 2 is the target monomer.



**Fig. 1** Relationship between Greenley's ( $Q_G, e_G$ ) and Young's ( $Q_Y, e_Y$ )  $Q$ - $e$  values for 82 monomers: (a)  $\ln Q_G$  vs  $\ln Q_Y$ , and (b)  $e_G$  vs  $e_Y$ . The dashed lines indicate the regression lines corresponding to (a)  $\ln Q_G = 0.984 \ln Q_Y - 0.149$  ( $r^2 = 0.834$ ), and (b)  $e_G = 0.988 e_Y + 0.050$  ( $r^2 = 0.715$ ).

The  $Q$ - $e$  scheme is a successful attempt to divide the reactivity ratio into nonpolar and polar contributions. More specifically, the  $Q$  value represents the general reactivity (nonpolar resonance effect) of the monomer, while the  $e$  value represents the polarity of the monomer (or radical). However, the scheme

still has some limitations, such as the assumption  $e_R = e_M$  and the arbitrariness in determining the  $e$  values. To overcome these limitations, several attempts have been made to improve the scheme.<sup>8,9</sup> The first attempt to treat the  $e$  parameter of a radical independently is the  $Q-e-e^*$  scheme proposed by Wall,<sup>10</sup> where  $e^*$  indicates the  $e$  value of the radical. Later, Hoyland<sup>11</sup> increased the number of monomers to obtain the  $Q-e-e^*$  parameters through statistical fitting. Although the accuracy of the predicted reactivity ratio was enhanced by the increased number of parameters, the physical meaning of the parameters was lost because of the arbitrariness in determining them.

In addition, Bamford et al.<sup>12</sup> non-arbitrarily determined the parameter that represents the polarity of a radical, which is related to the  $e$  value using the patterns of the reactivity scheme, and includes the general reactivity and polarity of a radical that are lost in the  $Q-e$  scheme. The general reactivity of a radical is measured by the transfer constant using toluene, and the polarity of a radical is measured by the Hammett constant,  $\sigma$ , for substituent(s) on the  $\alpha$ -carbon of the radical. Although the patterns scheme is claimed to be more accurate in predicting the reactivity ratios compared to the  $Q-e$  scheme, its use is limited because of its requirement to use the transfer constants and the Hammett constant.

In 1996, Jenkins<sup>13</sup> derived two pattern schemes revised according to theoretical and experimental considerations. In these schemes, the general reactivity of a radical was measured by the reactivity ratio of copolymerization with respect to (the nonpolar) styrene rather than using the transfer constants, and the polarity of the radical was measured by the difference between the reactivity ratios with respect to styrene and (the highly polar) acrylonitrile, rather than using the Hammett constants. The first scheme is known as the revised patterns U,V scheme:

$$\log r_{12} = \log r_{1S} - u_2\pi_1 - v_2, \quad (6)$$

$$\log r_{21} = \log r_{2S} - u_1\pi_2 - v_1, \quad (7)$$

where  $\log r_{1S}$  is the general reactivity of radical 1 with respect to styrene. The terms  $u_2$  and  $v_2$  are the polarity and general reactivity of monomer 2, respectively. The polar parameter corresponding to the Hammett constant of radical 1 is represented by  $\pi_1$ , which can be expressed by the reactivity ratios of radical 1 to styrene (S) and acrylonitrile (A):

$$\pi_1 = 0.385 \log(r_{1A}/0.377 r_{1S}). \quad (8)$$

The  $-u_2$  and  $-v_2$  values of monomer 2 are obtained from the slope and intercept by plotting  $(\log r_{12} - \log r_{1S})$  of a series of reference radical 1 against  $\pi_1$ , respectively. The parameters of various monomers are reported in the *Polymer Handbook*.<sup>14</sup> The second scheme was derived in the special case where the reference radicals are limited to styrene and acrylonitrile:

$$\log r_{12} = \log(r_{1S}r_{S2}) - \frac{\log(r_{AS}r_{S2}/r_{A2}) \log(r_{SA}r_{1S}/r_{1A})}{\log(r_{AS}r_{SA})}, \quad (9)$$

$$\log r_{21} = \log(r_{2S}r_{S1}) - \frac{\log(r_{AS}r_{S1}/r_{A1}) \log(r_{SA}r_{2S}/r_{2A})}{\log(r_{AS}r_{SA})}. \quad (10)$$

This scheme is called the revised patterns A,S scheme, where the reactivity ratio of radical copolymerization between monomers 1 and 2 can be predicted provided their reactivity ratios to styrene and acrylonitrile are known. In this scheme, the  $u$ ,  $v$ , and  $\pi$  parameters are no longer required, and the arbitrariness in the  $Q-e$  scheme disappears as a result. The revised patterns scheme has been used for uncommon monomer pairs, such as methyl vinyl ketone and methyl acrylate,<sup>15</sup> ethylene glycol dimethacrylate and 2-vinylpyridine,<sup>16</sup> 1H,1H,2H,2H-perfluorodecyl vinyl ether and vinylidene cyanide,<sup>17</sup> 2,2,2-trifluoroethyl methacrylate and vinylidene cyanide,<sup>18</sup> 2,2,2-trifluoroethyl acrylate and acrylonitrile,<sup>19</sup> glycidyl methacrylate and octadecyl acrylate,<sup>20</sup> and glycidyl methacrylate and methyl methacrylate.<sup>21</sup>

Although the schemes applied are different, the methods proposed by Greenley and Jenkins are similar in that they both use multiple reference monomers to determine the values of the parameters. Our approach is to use the reference reactivity ratios to express the  $Q-e$  parameters, rather than determining the  $Q-e$  values by fitting the reference reactivity ratios.

### Derivation of the intrinsic $Q-e$ scheme and expression of the individual radical and monomer $Q-e$ parameters using the intrinsic $Q-e$ parameters

We begin with the following  $Q-e$  scheme that extends the original schemes/equations (1) and (2) to include the  $Q-e$  parameters of individual monomers and radicals:

$$r_{12} = (Q_{R(1)}/Q_{M(2)}) \exp[-e_{R(1)}(e_{M(1)} - e_{M(2)})], \quad (11)$$

$$r_{21} = (Q_{R(2)}/Q_{M(1)}) \exp[-e_{R(2)}(e_{M(2)} - e_{M(1)})]. \quad (12)$$

The difference between these expressions and the original scheme is that the radical  $Q$  parameters ( $Q_R$ ) are included in the numerator of the pre-exponential factors. In addition, the radical  $e$  parameters ( $e_R$ ) are treated independently. We will refer to this representation as the generalized  $Q-e$  scheme. The validity for using such an expression will be discussed later. Applying Equations (11) and (12) to the monomer pairs among monomer 1, styrene (S), and acrylonitrile (A), leads to the following 6 equations:

$$r_{1S} = (Q_{R(1)}/Q_{M(S)}) \exp(-e_{R(1)}\delta_{M(1)}), \quad (13)$$

$$r_{S1} = (Q_{R(S)}/Q_{M(1)}) \exp(e_{R(S)}\delta_{M(1)}), \quad (14)$$

$$r_{1A} = (Q_{R(1)}/Q_{M(A)}) \exp[-e_{R(1)}(\delta_{M(1)} - \delta_{M(A)})], \quad (15)$$

$$r_{A1} = (Q_{R(A)}/Q_{M(1)}) \exp[e_{R(A)}(\delta_{M(1)} - \delta_{M(A)})], \quad (16)$$

$$r_{SA} = (Q_{R(S)}/Q_{M(A)}) \exp(e_{R(S)}\delta_{M(A)}), \quad (17)$$

$$r_{AS} = (Q_{R(A)}/Q_{M(S)}) \exp(-e_{R(A)}\delta_{M(A)}), \quad (18)$$

where the parameters,  $\delta_M$  and  $\delta_R$ , are introduced to simplify the subsequent notations representing the relative  $e$  values of a monomer and a radical with respect to styrene, respectively:

$$\delta_{M(1)} = e_{M(1)} - e_{M(S)}, \quad (19)$$

$$\delta_{R(1)} = e_{R(1)} - e_{R(S)}. \quad (20)$$

We assume that the monomer and radical  $Q$  parameters of styrene, i.e.,  $Q_{M(S)}$  and  $Q_{R(S)}$ , are equal to the constant  $Q_S$ :

$$Q_{M(S)} = Q_{R(S)} = Q_S. \quad (21)$$

Considering the natural logarithms of the different sides of Equations (13), (15), and (17), and combining them to eliminate the  $Q$  parameter using Equation (21), we obtain the following equation:

$$\ln r_{1S} - \ln r_{1A} + \ln r_{SA} = -e_{R(1)}\delta_{M(A)} + e_{R(S)}\delta_{M(A)} = -\delta_{R(1)}\delta_{M(A)}. \quad (22)$$

Similarly, the following equation can be obtained from Equations (14), (16), and (18):

$$\ln r_{S1} - \ln r_{A1} + \ln r_{AS} = e_{R(S)}\delta_{M(1)} - e_{R(A)}\delta_{M(1)} = -\delta_{R(A)}\delta_{M(1)}. \quad (23)$$

Transforming Equations (22) and (23) gives the expressions for  $\delta_{R(1)}$  and  $\delta_{M(1)}$ , respectively:

$$\delta_{R(1)} = \ln(r_{1A}/r_{1S}r_{SA})/\delta_{M(A)} = e_{R(1)}^\circ/\delta_{M(A)}, \quad (24)$$

$$\delta_{M(1)} = \ln(r_{A1}/r_{S1}r_{AS})/\delta_{R(A)} = e_{M(1)}^\circ/\delta_{R(A)}. \quad (25)$$

where the parameters  $e_{R(1)}^\circ$  and  $e_{M(1)}^\circ$  are defined by the following:

$$e_{R(1)}^\circ = \ln(r_{1A}/r_{1S}r_{SA}), \quad (26)$$

$$e_{M(1)}^\circ = \ln(r_{A1}/r_{S1}r_{AS}). \quad (27)$$

Furthermore,  $Q_{R_1}$  and  $Q_{M_1}$  can be calculated using the following equations obtained by transforming Equations (13) and (14), respectively:

$$Q_{R(1)} = r_{1S}Q_S \exp(e_{R(1)}\delta_{M(1)}) = Q_{R(1)}^\circ Q_S \exp(e_{R(1)}\delta_{M(1)}), \quad (28)$$

$$Q_{M(1)} = (Q_S/r_{S(1)}) \exp(e_{R(S)}\delta_{M(1)}) = Q_S Q_{M(1)}^\circ \exp(e_{R(S)}\delta_{M(1)}), \quad (29)$$

where the parameters  $Q_{R(1)}^\circ$  and  $Q_{M(1)}^\circ$  are introduced as:

$$Q_{R(1)}^\circ = r_{1S}, \quad (30)$$

$$Q_{M(1)}^\circ = 1/r_{S1}. \quad (31)$$

Substituting Equations (28) and (29) into Equation (11) and rearranging Equations (24) and (25), the reactivity ratio  $r_{12}$  can be expressed as follows:

$$\begin{aligned} r_{12} &= (Q_{R(1)}/Q_{M(2)}) \exp[-e_{R(1)}(\delta_{M(1)} - \delta_{M(2)})] \\ &= (Q_{R(1)}^\circ/Q_{M(2)}^\circ) \exp(e_{R(1)}\delta_{M(1)} - e_{R(S)}\delta_{M(2)}) \\ &\quad \times \exp[-e_{R(1)}(\delta_{M(1)} - \delta_{M(2)})] \\ &= (Q_{R(1)}^\circ/Q_{M(2)}^\circ) \exp(\delta_{R(1)}\delta_{M(2)}) \\ &= (Q_{R(1)}^\circ/Q_{M(2)}^\circ) \exp(e_{R(1)}^\circ e_{M(2)}^\circ/\delta_{M(A)}\delta_{R(A)}). \end{aligned} \quad (32)$$

In addition to the previous assumption for Equation (21), we also assume that the  $Q$  parameters of acrylonitrile,  $Q_{M(A)}$  and  $Q_{R(A)}$ , are equal to the constant  $Q_A$ :

$$Q_{M(A)} = Q_{R(A)} = Q_A. \quad (33)$$

This allows us to cancel the  $Q$  parameters from the product of the reactivity ratios,  $r_{AS}r_{SA}$ , i.e., the product of Equations (17) and (18), leading to the following simple expression:

$$r_{AS}r_{SA} = \exp(-\delta_{R(A)}\delta_{M(A)}). \quad (34)$$

Using this relationship, Equation (32) can be expressed as:

$$r_{12} = (Q_{R(1)}^\circ/Q_{M(2)}^\circ) \exp[-e_{R(1)}^\circ e_{M(2)}^\circ/\ln(r_{AS}r_{SA})]. \quad (35)$$

Similarly,  $r_{21}$  can be expressed in the following equation, which is symmetrical to Equation (35):

$$r_{21} = (Q_{R(2)}^\circ/Q_{M(1)}^\circ) \exp[-e_{R(2)}^\circ e_{M(1)}^\circ/\ln(r_{AS}r_{SA})]. \quad (36)$$

Since all the parameters included here are expressed in terms of the reactivity ratios between the target and the reference monomers, the reactivity ratio between the target monomer pairs can be predicted without arbitrariness. Moreover, it is worth noting that the only assumption required to derive this scheme is that the conjugate monomer and the radical  $Q$  values of the reference monomer are equal, i.e.,  $Q_{M(S)} = Q_{R(S)}$  and  $Q_{M(A)} = Q_{R(A)}$ . Since the reactivity ratio between the target monomer pairs can be predicted by using only the reference reactivity ratios without arbitrariness, an assumption such as  $e_R = e_M$ , and setting the reference  $Q$ - $e$  values, the expression of the reactivity ratios in Equations (35) and (36) can be referred to as the intrinsic  $Q$ - $e$  scheme, and  $Q_{R(1)}^\circ$ ,  $Q_{M(1)}^\circ$ ,  $e_{R(1)}^\circ$ , and  $e_{M(1)}^\circ$  are the intrinsic  $Q$ - $e$  parameters.

To understand the physical meaning of the intrinsic  $Q_{R(1)}^\circ$  and  $Q_{M(1)}^\circ$  parameters, they are expressed in terms of rate constants:

$$Q_{R(1)}^\circ = k_{11}/k_{1S}, \quad (37)$$

$$Q_{M(1)}^\circ = k_{S1}/k_{SS}. \quad (38)$$

These parameters represent the relative reactivity of the conjugate radical and monomer 1 with respect to styrene,

respectively. On the other hand, the intrinsic parameters  $e_{R_1}^\circ$  and  $e_{M_1}^\circ$  are expressed in terms of rate constants as follows:

$$e_{R(1)}^\circ = \ln[(k_{1S}/k_{1A})/(k_{SS}/k_{SA})], \quad (39)$$

$$e_{M(1)}^\circ = \ln[(k_{S1}/k_{A1})/(k_{SS}/k_{AS})]. \quad (40)$$

Since these intrinsic parameters are functions of the ratio of the rate constants for the polar acrylonitrile and the nonpolar styrene, respectively, they provide an indication of the polarity of the conjugated radical and monomer 1. This is also supported by the fact that the  $e$  values of the monomers obtained from the intrinsic  $e$  parameters correlate well with Greenley's  $e$  values, which are known to represent polarity, as discussed below. When the conjugate radical and monomer 1 are both styrene, the following equation holds true:

$$e_{R(S)}^\circ = e_{M(S)}^\circ = 0. \quad (41)$$

Moreover, when the conjugate radical and monomer 1 are both acrylonitrile, the following equation holds:

$$e_{R(A)}^\circ = e_{M(A)}^\circ = -\ln(r_{AS}r_{SA}). \quad (42)$$

Therefore, the intrinsic  $e$  parameters ( $e_{R(1)}^\circ$  and  $e_{M(1)}^\circ$ ) are symmetrical representations with scales equivalent to one another.

Finally, the  $Q$ - $e$  parameters of individual radicals and monomers can be expressed in terms of the intrinsic  $Q$ - $e$  parameters, i.e., the  $e$  parameters of the conjugate radical and monomer 1,  $e_{R(1)}^\circ$  and  $e_{M(1)}^\circ$ , can be expressed by the intrinsic  $e_{R(1)}^\circ$  and  $e_{M(1)}^\circ$  parameters, transformed from Equations (24) and (25), respectively:

$$e_{R(1)} = e_{R(S)} + (e_{R(1)}^\circ/\delta_{M(A)}), \quad (43)$$

$$e_{M(1)} = e_{M(S)} + (e_{M(1)}^\circ/\delta_{R(A)}). \quad (44)$$

The  $Q_{R(1)}$  and  $Q_{M(1)}$  values of the conjugate radical and monomer 1 can be expressed by substituting Equations (43) and (44) into Equations (28) and (29), respectively:

$$Q_{R(1)} = Q_S \exp\{[e_{R(S)} + (e_{R(1)}^\circ/\delta_{M(A)})](e_{M(1)}^\circ/\delta_{R(A)})\}, \quad (45)$$

$$Q_{M(1)} = Q_S Q_{M(1)}^\circ \exp(e_{R(S)} e_{M(1)}^\circ/\delta_{R(A)}). \quad (46)$$

The radical ( $e_{R(1)}$ ) and monomer ( $e_{M(1)}$ ) parameters are related to the intrinsic parameters  $e_{R(1)}^\circ$  and  $e_{M(1)}^\circ$  through Equations

(43) and (44), which indicate the polarities of the radical and monomer, respectively. However, since the radical and monomer  $Q$  parameters ( $Q_{R(1)}$  and  $Q_{M(1)}$ ) are expressed by the intrinsic parameters ( $Q_{R(1)}^\circ$  and  $Q_{M(1)}^\circ$ ) corrected with the intrinsic parameters ( $e_{R(1)}^\circ$  and  $e_{M(1)}^\circ$ ) as shown in Equations (45) and (46), the meaning of the  $Q$  value is different from that of the intrinsic  $Q$  value, i.e., the  $Q_{R(1)}^\circ$  and  $Q_{M(1)}^\circ$  values indicate the general reactivities of radical 1 and monomer 1, respectively, while the  $Q_{R_1}$  and  $Q_{M_1}$  values may indicate the resonance effect of radical 1 and monomer 1, respectively.

The radical and monomer  $Q$ - $e$  values can be individually calculated using Equations (43)–(46) with the reactivity ratios of the target monomer with respect to the reference monomers, in addition to the given  $Q_S$ ,  $e_{M(S)}$ ,  $e_{R(S)}$ ,  $e_{M(A)}$ , and  $e_{R(A)}$  reference values. It is noteworthy that setting these reference values is optional and changing them does not affect the predicted values of the reactivity ratio. The reason for this is that since the monomer and radical  $Q$ - $e$  parameters are expressed by the intrinsic parameters, the reactivity ratio calculated using these parameters with the generalized  $Q$ - $e$  scheme is in agreement with that calculated by the intrinsic  $Q$ - $e$  scheme. Alfrey and Price initially set the  $e$  value of styrene to  $-1$ ,<sup>1</sup> and later Price revised it to  $-0.8$ .<sup>2</sup> Moreover, setting the  $e$  value to zero for styrene<sup>22</sup> and ethylene<sup>23</sup> has also been proposed. However, there is no physical significance in setting the  $Q$ - $e$  values of the reference monomers, at least in our case, as they are simply the reference values used for determining the radical and monomer  $Q$ - $e$  values.

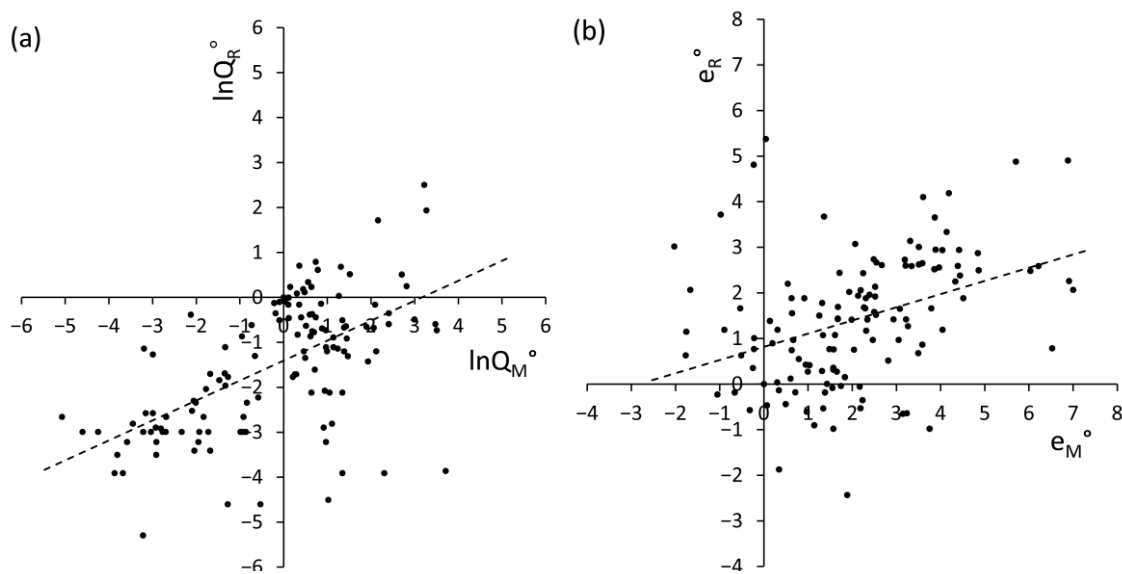
### Calculation examples for individual radical and monomer $Q$ - $e$ values

Initially, the intrinsic  $Q$ - $e$  parameters were calculated using the reactivity ratios of 143 monomers with styrene and acrylonitrile as references, which were taken from the *Polymer Handbook*.<sup>14</sup> The reactivity ratios used in the revised patterns scheme were selected by Jenkins from Greenley's reactivity ratio data table in the *Polymer Handbook*.<sup>24</sup> The reactivity ratios between styrene and acrylonitrile ( $r_{AS} = 0.04$  and  $r_{SA} = 0.38$ ) were also used for the purpose of these calculations. The calculated results for the 15 selected monomers and the reactivity ratios used for the calculations are summarized in Table 1; the data for all monomers are provided in Table S1. To verify the correlations among the intrinsic  $Q$ - $e$  values,  $\ln Q_{R(1)}^\circ$  vs  $\ln Q_{M(1)}^\circ$  and  $e_{R(1)}^\circ$  vs  $e_{M(1)}^\circ$  values, plotted in Figs. 2(a) and 2(b), respectively, wherein dispersion can be observed without any clear correlation ( $r^2 = 0.341$  and  $0.145$ , respectively).

**Table 1** Reactivity ratios with respect to styrene and acrylonitrile ( $r_{1S}$ ,  $r_{1A}$ ,  $r_{A1}$ ,  $r_{S1}$ )<sup>a</sup>, and intrinsic  $Q$ - $e$  parameters ( $Q_M^\circ$ ,  $Q_R^\circ$ ,  $e_M^\circ$ ,  $e_R^\circ$ )

Monomer	$r_{1S}$	$r_{1A}$	$r_{A1}$	$r_{S1}$	$Q_M^\circ$	$Q_R^\circ$	$e_M^\circ$	$e_R^\circ$
Styrene (S): reference	1	0.38	0.04	1	1	1	0	0
Acrylonitrile (A): reference	0.04	1	1	0.38	2.63	0.04	4.19	4.19
Butadiene (B)	1.40	0.29	0.06	0.57	1.75	1.40	0.97	-0.61
2-Chlorobutadiene (2CB)	6.91	5.18	0.05	0.04	26.3	6.91	3.49	0.68
Isoprene (I)	1.84	0.45	0.03	0.46	2.18	1.84	0.49	-0.44
Maleic anhydride (MAN)	0.01	0.05	6	0.36	2.78	0.01	6.03	2.48
Methacrylic acid (MAc)	0.52	0.2	0.04	0.24	4.17	0.52	1.43	0.00
Methacrylonitrile (MAN)	0.33	1.67	0.43	0.38	2.63	0.33	3.34	2.59
Methyl acrylate (MA)	0.18	0.85	1.42	0.75	1.33	0.18	3.86	2.52
Methyl methacrylate (MMA)	0.46	1.32	0.14	0.5	2.00	0.46	1.93	2.02
Vinyl acetate (VA)	0.02	0.05	4.78	48	0.02	0.02	0.91	1.88
	(0.04)	(0.04)	(4.05)	(18.8)	(0.05)	(0.04)	(1.68)	(0.97)
Vinyl chloride (VC)	0.06	0.05	3.29	18.7	0.05	0.06	1.48	0.77
	(0.06)	(0.07)	(2.55)	(12.4)	(0.08)	(0.06)	(1.64)	(1.21)
Vinyl ethyl ether (VEE)	0.05	0.06	0.69	100	0.01	0.05	-1.76	1.15
2-Vinyl pyridine (2VP)	1.26	0.44	0.10	0.53	1.89	1.26	1.55	-0.08
Vinylidene chloride (VDC)	0.11	0.32	0.64	1.79	0.56	0.11	2.19	2.06

<sup>a</sup>Reactivity ratios were taken from the *Polymer Handbook*.<sup>14</sup> The values shown in italics and in parentheses correspond to those calculated using the different reference reactivity ratios for VA and VC.



**Fig. 2** Relationship between the intrinsic  $Q$ - $e$  parameters for 143 monomers: (a)  $\ln Q_R^\circ$  vs  $\ln Q_M^\circ$  and (b)  $e_R^\circ$  vs  $e_M^\circ$ . The dashed lines indicate the regression lines corresponding to (a)  $\ln Q_R^\circ = 0.444 \ln Q_M^\circ - 1.408$  ( $r^2 = 0.341$ ) and (b)  $e_R^\circ = 0.289 e_M^\circ + 0.817$  ( $r^2 = 0.145$ ).

Furthermore, to calculate the  $Q$ - $e$  values of the individual radicals and monomers using Equations (43)–(46) and the calculated intrinsic parameters, the monomer and radical  $Q$ - $e$  values of the reference monomer should be set. Here, the following settings were chosen such that the calculated  $Q$ - $e$  values can be compared to the accumulated  $Q$ - $e$  values. Price's  $Q$ - $e$  values<sup>2</sup> were adopted for styrene ( $Q_S = 1$ ,  $e_{M(S)} = e_{R(S)} = -0.8$ ) and Greenley's values<sup>6</sup> were selected for the  $e$  value of acrylonitrile ( $e_{M(A)} = e_{R(A)} = 1.23$ , that is,  $\delta_{M(A)} = \delta_{R(A)} = 2.03$ ). Substituting these values into Equations (43)–(46) provides the following expressions:

$$e_{R(1)} = -0.8 + \frac{1}{2.03} \ln \frac{r_{1A}}{0.38r_{1S}}, \quad (43')$$

$$e_{M(1)} = -0.8 + \frac{1}{2.03} \ln \frac{r_{A1}}{0.04r_{S1}}, \quad (44')$$

$$Q_{R(1)} = r_{1S} \exp \left\{ \left[ -0.8 + \frac{\ln(r_{1A}/0.38r_{1S})}{2.03} \right] \left[ \frac{\ln(r_{A1}/0.04r_{S1})}{2.03} \right] \right\}, \quad (45')$$

$$Q_{M(1)} = \frac{1}{r_{S1}} \exp \left[ \frac{-0.8 \ln(r_{A1}/0.04r_{S1})}{2.03} \right]. \quad (46')$$

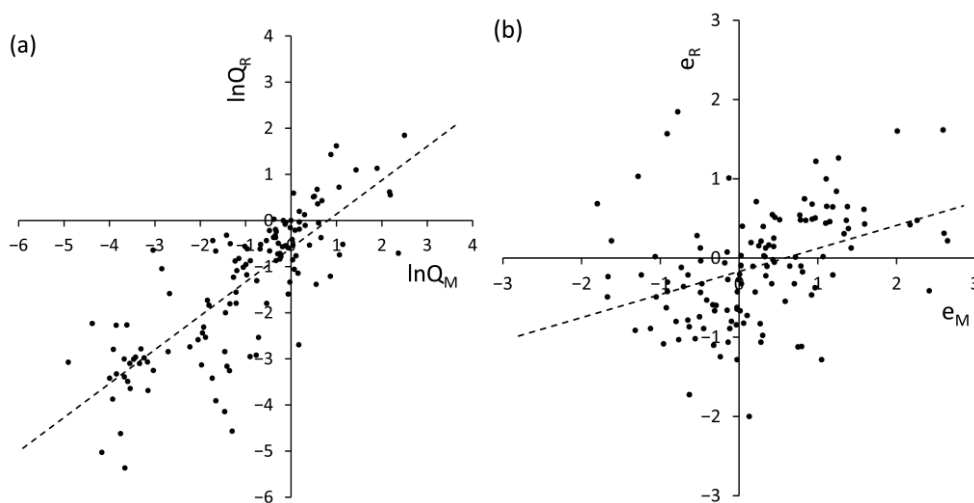
Thus, the radical and monomer  $Q$ - $e$  values can be calculated using the reactivity ratios listed in Table 1 or Table S1. The calculated  $Q$ - $e$  values for the selected monomers are listed in Table 2, and the data for all 143 monomers are provided in Table S2. In addition, the plot of  $\ln Q_R$  vs  $\ln Q_M$  for all monomers is shown in Fig. 3(a), wherein it can be seen that the radical and monomer  $Q$  values are relatively correlated ( $r^2 = 0.637$ ), and the deviations from  $Q_R = Q_M$  are particularly large for methyl  $\alpha$ -cyanoacrylate ( $|Q_M - Q_R| = 10.11$ ), methacryloylacetone (7.14), itaconic anhydride (6.89), trans-4-ethoxy-2,4-diethyl pentadienoate (5.80), and 2-chlorobutadiene (3.54). The plot of  $e_R$  vs  $e_M$  for all monomers is shown in Fig. 3(b), wherein a

scattered plot can be observed, and the radical and monomer  $e$  values are not correlated ( $r^2 = 0.147$ ). Furthermore, some of the  $e$  values either do not follow  $e_R = e_M$  or have different signs. Therefore, the assumption of the  $Q$ - $e$  scheme,  $e_R = e_M$ , does not hold in many cases. Large deviations from  $e_R = e_M$  were found for diethyl fumarate ( $|e_M - e_R| = 2.83$ ), ferrocenyl methyl methacrylate (2.63), acenaphthalene (2.49), 2,2,6,6-tetramethyl-4-piperidinyl methacrylate (2.48), ethyl  $\alpha$ -cyanoacrylate (2.43), crotonaldehyde (2.33),  $N$ -vinyl succinimide (2.31), diisopropyl fumarate (2.29), and 3-tri- $n$ -butylstannyl styrene, and 34 monomers possessed different signs between  $e_R$  and  $e_M$ . It is interesting to note that the correlation between the  $Q$  values of the radicals and monomers ( $r^2 = 0.637$ ) becomes higher than between the intrinsic  $Q$  parameters ( $r^2 = 0.341$ ). This indicates that the meanings of both parameters are different, as noted earlier.

**Table 2.**  $Q$ - $e$  parameters for the monomers and radicals ( $Q_M$ ,  $Q_R$ ,  $e_M$ ,  $e_R$ ), Greenley's  $Q$ - $e$  Values ( $Q_G$ ,  $e_G$ ), and Young's  $Q$ - $e$  Values ( $Q_Y$ ,  $e_Y$ )<sup>a</sup>

Monomer	$Q_M$	$Q_R$	$e_M$	$e_R$	$Q_G$	$e_G$	$Q_Y$	$e_Y$
S	1	1	-0.8	-0.8	1	-0.8	1	-0.8
A	0.51	0.54	1.26	1.26	0.48	1.23	0.6	1.2
B	1.20	0.83	-0.32	-1.10	1.7	-0.5	2.39	-1.05
2CB	6.64	3.10	0.92	-0.47	10.5	1.2	7.26	-0.02
I	1.80	1.44	-0.56	-1.02	1.99	-0.55	3.33	-1.22
MAN	0.26	0.04	2.17	0.42	0.86	3.69	0.23	2.25
MAc	2.37	0.30	-0.10	-0.80	0.98	0.62	2.34	0.65
MAN	0.70	0.72	0.85	0.48	0.86	0.68	1.12	0.81
MA	0.29	0.42	1.10	0.44	0.45	0.64	0.42	0.6
MMA	0.93	0.55	0.15	0.20	0.78	0.4	0.74	0.4
VA	0.01	0.02	-0.35	0.13	0.03	-0.88	0.026	-0.22
	<i>(0.03)</i>	<i>(0.03)</i>	<i>(0.03)</i>	<i>(-0.32)</i>				
VC	0.03	0.04	-0.07	-0.42	0.06	0.16	0.044	0.2
	<i>(0.04)</i>	<i>(0.05)</i>	<i>(0.01)</i>	<i>(-0.20)</i>				
VEE	0.02	0.06	-1.67	-0.23	0.02	-1.8	0.032	-1.17
2VP	1.02	0.66	-0.04	-0.84	1.41	-0.42	1.3	-0.5
VDC	0.24	0.14	0.28	0.21	0.31	0.34	0.22	0.36

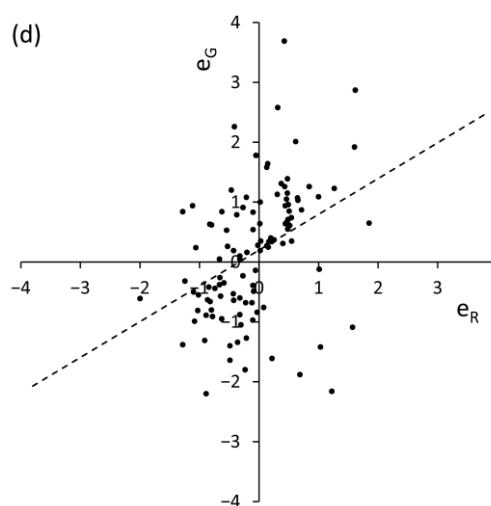
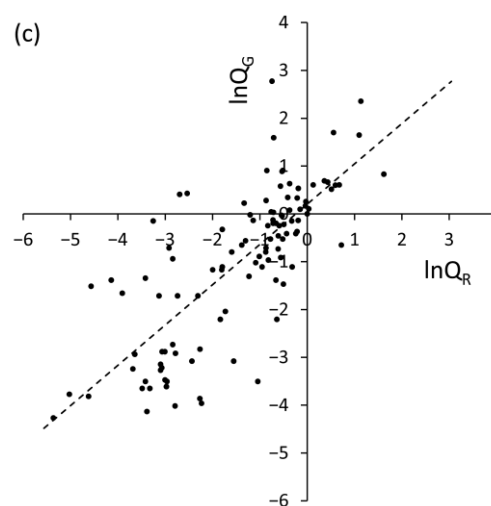
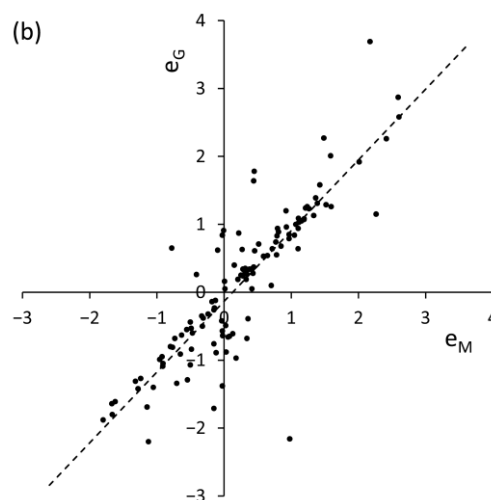
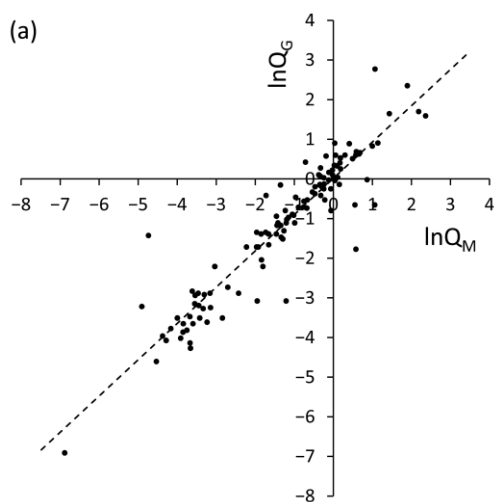
<sup>a</sup>For the monomer abbreviations, please refer to Table 1. The values represented in italics and in parentheses correspond to those calculated using the different reference reactivity ratios for VA and VC, as indicated in Table 1. Greenley's and Young's  $Q$ - $e$  values were taken from the *Polymer Handbook*.<sup>5,5</sup>





**Fig. 3** Relationship between the radical and monomer  $Q$ - $e$  parameters for 143 monomers: (a)  $\ln Q_R$  vs  $\ln Q_M$  and (b)  $e_R$  vs  $e_M$ . The dashed lines indicate the regression lines corresponding to (a)  $\ln Q_R = 0.735 \ln Q_M - 0.597$  ( $r^2 = 0.637$ ) and (b)  $e_R = 0.291 e_M - 0.170$  ( $r^2 = 0.147$ ).

The correlations between the monomer and radical  $Q$ - $e$  values and Greenley's  $Q$ - $e$  values ( $Q_G$ - $e_G$ ) were then examined. As shown in Figs. 4(a) and 4(b), good correlations exist between  $\ln Q_M$  and  $\ln Q_G$ , and  $e_M$  and  $e_G$  ( $r^2 = 0.870$  and  $0.747$ ), respectively. On the other hand, as shown in Figs. 4(c) and 4(d), there is a slight correlation between the radical ( $\ln Q_R$ ) and Greenley's ( $\ln Q_G$ )  $Q$  values ( $r^2 = 0.583$ ), while there is no correlation between the radical ( $e_R$ ) and Greenley's ( $e_G$ )  $e$  values ( $r^2 = 0.149$ ). The correlations between the monomer and radical  $Q$ - $e$  values and Young's  $Q$ - $e$  values ( $Q_Y$ - $e_Y$ ) were also examined. As shown in Fig. S1 of the Supporting Information, the correlations between the monomer and radical  $Q$ - $e$  values with Young's  $Q$ - $e$  values are close to those obtained using Greenley's  $Q$ - $e$  values. However, the  $e_M$  and  $e_G$  values are slightly lower in the case of Young's values ( $r^2 = 0.638$ ) compared to those in the case of Greenley's values ( $r^2 = 0.747$ ) despite the correlation between  $\ln Q_M$  and  $\ln Q_G$  being comparable for the two cases (Young's values,  $r^2 = 0.840$ ; Greenley's values,  $r^2 = 0.870$ ). These observations suggest that the monomer  $Q$ - $e$  values were successfully extracted, while Young's  $e$  values are the mean properties of the conjugate radical and monomer. Therefore, we can say that the  $Q_M$ - $e_M$  values obtained here reasonably correspond to the monomer properties. The slight discrepancy between the  $Q_M$ - $e_M$  and  $Q_G$ - $e_G$  values can be attributed to the fact that Greenley used three or more reference monomers, while in the intrinsic  $Q$ - $e$  scheme only two reference monomers were used. Since there is no direct data to be compared with the radical  $Q_R$ - $e_R$  values, the  $e$  values of butadiene (B), 2-chlorobutadiene (2CB), and isoprene (I) with diene skeletons (see Table 2) were examined. As indicated, these species exhibited larger negative  $e$  values in their radical values ( $e_R = -1.10, -0.47, -1.02$ ) than in their monomer  $e$  values ( $e_M = -0.32, 0.92, -0.56$ ). This is consistent with the expected high donor nature of the allyl radicals, since these diene monomers form allyl radicals.



**Fig. 4** Relationship between the  $Q$ - $e$  values for a monomer ( $Q_M, e_M$ ) and a radical ( $Q_R, e_R$ ), and Greenley's  $Q$ - $e$  values ( $Q_G, e_G$ ) for 111 monomers: (a)  $\ln Q_G$  vs  $\ln Q_M$ , (b)  $e_G$  vs  $e_M$ , (c)  $\ln Q_G$  vs  $\ln Q_R$ , and (d)  $e_G$  vs  $e_R$ . The dashed lines indicate the regression lines corresponding to (a)  $\ln Q_G = 0.915 \ln Q_M + 0.015$  ( $r^2 = 0.870$ ), (b)  $e_G = 1.041 e_M - 0.134$  ( $r^2 = 0.747$ ), (c)  $\ln Q_G = 0.842 \ln Q_R + 0.202$  ( $r^2 = 0.583$ ), and (d)  $e_G = 0.598 e_R + 0.199$  ( $r^2 = 0.149$ ).

### Comparison of the intrinsic $Q$ - $e$ scheme with the revised patterns scheme

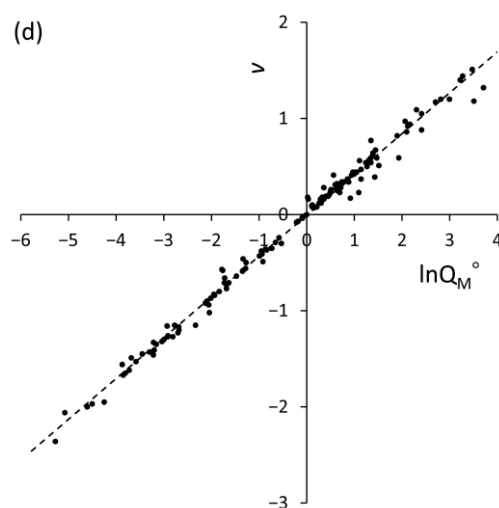
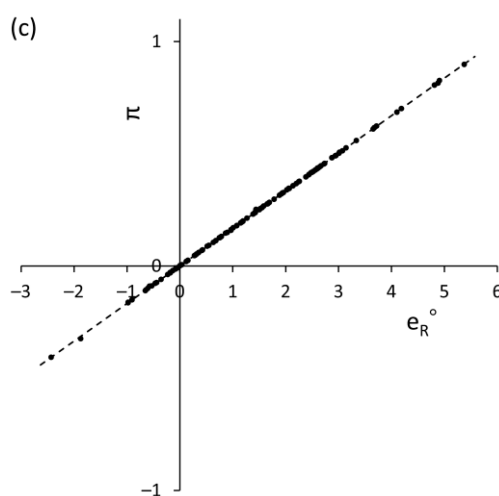
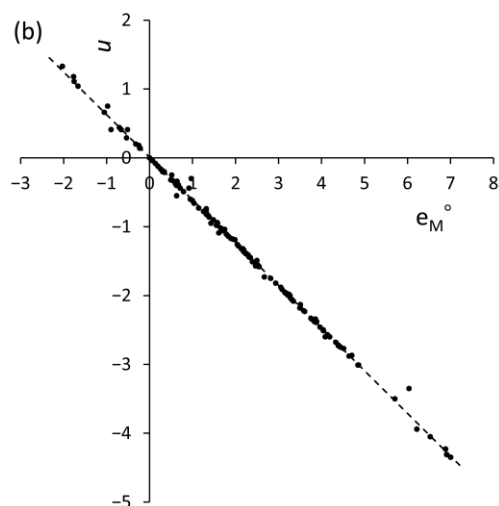
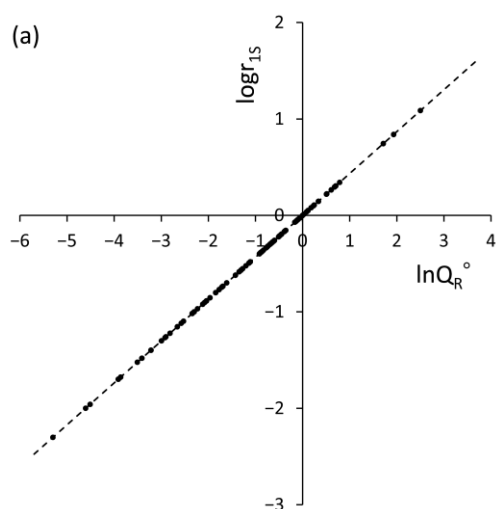
Substituting the equations of the four intrinsic parameters, namely Equations (26), (27), (30), and (31), into Equations (35) and (36) results in the following equations:

$$r_{12} = r_{1S} r_{S2} \exp[-\ln(r_{1A}/r_{1S} r_{SA}) \ln(r_{A2}/r_{S2} r_{AS}) / \ln(r_{AS} r_{SA})], \quad (47)$$

$$r_{21} = r_{2S} r_{S1} \exp[-\ln(r_{2A}/r_{2S} r_{SA}) \ln(r_{A1}/r_{S1} r_{AS}) / \ln(r_{AS} r_{SA})]. \quad (48)$$

Interestingly, these equations are mathematically equivalent to Equations (9) and (10) of the revised patterns A,S schemes, despite using different approaches.

To confirm the relationship between the intrinsic  $Q$ - $e$  and the revised patterns schemes, the parameters of the U,V scheme, including  $\log r_{1S}$ ,  $v$ ,  $\pi$ , and  $u$  (as extracted from the *Polymer Handbook*<sup>14</sup>), were plotted against the intrinsic  $Q$ - $e$  parameters,  $\ln Q_{R(1)}^\circ$ ,  $\ln Q_{M(1)}^\circ$ ,  $e_{R(1)}^\circ$ , and  $e_{M(1)}^\circ$ , respectively (see Fig. 5). Since  $\log r_{1S}$  and  $\ln Q_{R(1)}^\circ$ , and  $\pi$  and  $e_{R(1)}^\circ$  are mathematically equivalent to one another, it is natural that they show complete linearity ( $r^2 = 1.000$ ), as can be seen in Figs. 5(a) and 5(c). Furthermore,  $v$  vs  $\ln Q_{M(1)}^\circ$  and  $u$  vs  $e_{M(1)}^\circ$  also show fairly good linearities ( $r^2 = 0.998$  and  $0.992$ ) (Figs. 5(b) and 5(d)), although they are not necessarily equivalent. This is because unlike  $Q_{M(1)}^\circ$  and  $e_{M(1)}^\circ$ ,  $v$  and  $u$  were obtained from the plots against  $\pi$  for several radicals. These results clearly indicate that the intrinsic  $Q$ - $e$  parameters are consistent with the parameters of the revised patterns U,V scheme. It is therefore apparent that the intrinsic  $Q$ - $e$  and revised patterns schemes are equivalent. However, unlike the revised patterns scheme, the intrinsic  $Q$ - $e$  parameters can provide the  $Q$ - $e$  values of individual radicals and monomers.



**Fig. 5** Relationship between the intrinsic  $Q$ - $e$  parameters and the revised patterns U,V parameters for 143 monomers: (a)  $\log r_{1S}$  vs  $\ln Q_R^\circ$ , (b)  $u$  vs  $\ln Q_M^\circ$ , (c)  $\pi$  vs  $e_R^\circ$ , and (d)  $v$  vs  $e_M^\circ$ . The dashed lines indicate the regression lines corresponding to (a)  $\log r_{1S} = 0.434 \ln Q_R^\circ$  ( $r^2 = 1.000$ ), (b)  $u = 0.620 \ln Q_M^\circ + 0.008$  ( $r^2 = 0.998$ ), (c)  $\pi = 0.167 e_R^\circ$  ( $r^2 = 1.000$ ), and (d)  $v = 0.425 e_M^\circ + 0.007$  ( $r^2 = 0.992$ ).

## Accuracy of the reactivity ratios predicted by the intrinsic $Q$ - $e$ scheme

To examine the reactivity ratios predicted by the  $Q$ - $e$  scheme and the intrinsic  $Q$ - $e$  scheme in detail, we selected 19 monomer pairs, excluding styrene and acrylonitrile, from the monomer pairs used by Jenkins to verify the prediction accuracy of the revised patterns scheme.<sup>13,25</sup> The  $Q$ - $e$  values reported by Greenley<sup>6</sup> and Young<sup>5</sup> were also used to calculate the reactivity ratios. The results obtained are summarized in Table 3. We confirmed that the reactivity ratios calculated by the intrinsic  $Q$ - $e$  scheme and the  $Q$ - $e$  scheme using Greenley's  $Q$ - $e$  values reproduced the values reported by Jenkins. The mean absolute errors (MAEs) listed in Table 3 (denoted as MAE0) indicate that the intrinsic  $Q$ - $e$  scheme gave a higher MAE (i.e., 3.79) compared to the corresponding values of 1.59 (Greenley) and 1.96 (Young) for the  $Q$ - $e$  scheme. This is because the error in  $r_{12}$  is significantly larger when monomer 2 is vinyl acetate (VA) or vinyl chloride (VC). Therefore, the MAE was recalculated by excluding the value of  $r_{12}$  when monomer 2 was VA or VC. As a result, the MAE for the intrinsic  $Q$ - $e$  scheme was 0.22, which is a significant improvement, while the MAEs for the  $Q$ - $e$  values reported by Greenley and Young were 0.89 and 0.87, respectively. Thus, the accuracy of the intrinsic  $Q$ - $e$  scheme (including the revised patterns scheme) was found to be excellent for monomers other than VA and VC.

Since VA and VC are both classified as unconjugated monomers with small  $Q$ -values, and since they can be easily homopolymerized (i.e.,  $k_{11} > k_{12}$ ),  $r_{12}$  is generally large values when VA or VC is used as monomer 2. In addition, the values of  $r_{A1}$  and  $r_{S1}$  of VA and VC vary depending on the experiments, and the variation in  $r_{S1}$  is particularly large ( $r_{S1} = 37 \pm 28.59$  for VA,  $15.77 \pm 3.17$  for VC, while  $r_{A1} = 4.99 \pm 0.82$  for VA,  $3.22 \pm 0.56$  for VC).<sup>4</sup> Therefore, we recalculated the reactivity ratios for the monomer pairs including VA or VC as monomer 2 using the intrinsic  $Q$ - $e$  scheme with another reference data set possessing smaller  $r_{S1}$  and  $r_{A1}$  values, as specified within the parentheses in Table 1. Therefore, while improvements were observed, they were limited; the recalculated MAE (denoted as MAE2 in Table 3) was determined to be 1.57, which is comparable to the values of Greenley (1.59) and Young (1.96). Therefore, the poor accuracy of the intrinsic  $Q$ - $e$  scheme for the systems containing VA and VC is mainly due to the accuracy of the reactivity ratios employed. Such a prediction is considered to be difficult in terms of the original<sup>4</sup> and intrinsic  $Q$ - $e$  schemes, respectively. Although vinylidene chloride (VDC) is also an unconjugated monomer, unlike VA and VC, the  $r_{12}$  values predicted by the intrinsic  $Q$ - $e$  scheme for MMA/VDC, MA/VDC, and MAN/VDC are acceptable comparable to those of Greenley and superior to those of Young. This may be due to the fact that the monomer and radical  $Q$  values (0.24 and 0.14) of VDC are somewhat larger than those of VA and VC. Therefore, care must

be taken when applying the intrinsic  $Q$ - $e$  scheme to a system consisting of unconjugated monomers with small  $Q$ -values, such as VA and VC. Instead, it is better to consider it as only a qualitative prediction for the system containing unconjugated monomers. Furthermore, the 2-chlorobutadiene (2CB)/2-vinylpyridine (2VP) monomer pair was highlighted by Jenkins as an example where the revised patterns scheme gave more accurate predictions than Greenley's  $Q$ - $e$  values.<sup>25</sup> As can be seen in Table 3, for  $r_{12}$ , the intrinsic  $Q$ - $e$  scheme (4.71) agrees better with the experimental value (5.19) than when Greenley's value (1.07) is employed. However, a good agreement was also found when Young's value was considered (5.64). To examine the reasons for such different predictions, we divided the  $Q$ - $e$  scheme into the pre-exponential nonpolar  $Q$  factor ( $f_Q$ ) and the exponential polar  $e$  factor ( $f_e$ ) contributions, such as  $f_Q(r_{12}) = (Q_{M(1)}/Q_{M(2)})$  and  $f_e(r_{12}) = \exp[-e_{M(1)}(e_{M(1)} - e_{M(2)})]$ , respectively, for the  $Q$ - $e$  scheme. We also employed the  $Q$  and  $e$  factors of the generalized  $Q$ - $e$  scheme ( $f_Q^g(r_{12}) = (Q_{R(1)}/Q_{M(2)})$ ,  $f_e^g(r_{12}) = \exp[-e_{R(1)}(e_{M(1)} - e_{M(2)})]$ ) instead of the intrinsic  $Q$ - $e$  scheme. This is because  $f_Q^g$  and  $f_e^g$  could be directly compared to  $f_Q$  and  $f_e$ , respectively, and regardless of the generalized  $Q$ - $e$  scheme or the intrinsic  $Q$ - $e$  scheme, the predictions do not differ from one another within the numerical error. Since the values of both the  $Q$  and  $e$  factors are comparable in both schemes for  $r_{21}$  ( $f_Q(\text{Greenley}) = 0.13$  and  $f_e(\text{Greenley}) = 0.51$ ,  $f_Q(\text{Young}) = 0.18$  and  $f_e(\text{Young}) = 0.79$  for the  $Q$ - $e$  scheme, and  $f_Q^g = 0.10$  and  $f_e^g = 0.45$  for the generalized  $Q$ - $e$  scheme), it was apparent that the predictions would not have changed significantly. In contrast, for  $r_{12}$ ,  $f_Q(\text{Greenley}) = 7.46$  is 2.5 times larger than  $f_Q^g = 3.03$ ; conversely,  $f_e(\text{Greenley}) = 0.14$  is approximately 11 times smaller than  $f_e^g = 1.56$ , and  $f_Q(\text{Young}) = 5.58$  and  $f_e(\text{Young}) = 1.01$  are close to the values of  $f_Q^g$  and  $f_e^g$ , respectively. This indicates that the polar  $e$  factor plays an important role in determining the reactivity ratio in this case. As can be seen in Table 2, this is mainly due to the distinct monomer and radical  $e$  values ( $e_M$  and  $e_R$ ) for 2CB. More specifically, the  $e_M$  and  $e_R$  values have different signs;  $e_M = 0.92$  and  $e_R = -0.47$ , and thus,  $e_R = e_M$  is not valid. However, Young's value,  $e_Y = -0.02$ , is close to the mean value between  $e_R$  and  $e_M$ . In contrast, for Greenley's  $e$  value,  $e_G = 1.2$ , since this value indicates only the monomer property, while the Young's  $e$  value is the mean contribution from the monomer and radical, as mentioned earlier. As described previously, 2CB forms an allyl radical, which suggests that the polarity is different between the monomer and the radical, and the difference between  $Q_M$  and  $Q_R$  is also large (3.54), thereby indicating that the resonance effect may also be different between these species. Therefore, Greenley's  $Q$ - $e$  value is likely not suitable for predicting the reactivity ratio of a system consisting of diene monomers, such as 2CB, where the radical and monomer have different properties.

## ARTICLE

Table 3. Reactivity ratios predicted by the *Q-e* scheme using Greenley's ( $Q_G-e_G$ ) and Young's ( $Q_Y-e_Y$ ) *Q-e* values. Reactivity ratios predicted by the intrinsic *Q-e* Scheme (i*Q-e*). The experimentally obtained reactivity ratios (Exp.) with absolute errors ( $\Delta E$ ) and mean absolute errors (MAE) are also listed

Monomer Pair 1/2		Exp.	$Q_G-e_G$	$\Delta E$	$Q_Y-e_Y$	$\Delta E$	i <i>Q-e</i>	$\Delta E$
MMA/B	$r_{12}$	0.30	0.32	0.02	0.17	0.13	0.42	0.12
	$r_{21}$	0.65	1.39	0.74	0.70	0.05	0.53	0.12
MMA/I	$r_{12}$	0.26	0.27	0.01	0.12	0.14	0.27	0.01
	$r_{21}$	0.64	1.51	0.87	0.62	0.02	0.75	0.11
MMA/MA	$r_{12}$	2.15	1.91	0.24	1.91	0.24	2.22	0.07
	$r_{21}$	0.4	0.49	0.09	0.50	0.10	0.29	0.11
MMA/MAN	$r_{12}$	0.75	1.01	0.26	0.78	0.03	0.88	0.13
	$r_{21}$	0.50	0.91	0.41	1.09	0.59	0.54	0.04
MMA/VA	$r_{12}$	25	18.0	7.0	22.2	2.8	34	9
	$r_{21}$	0.04	0.01	0.03	0.03	0.01	(20)	(5)
MMA/VC	$r_{12}$	9.0	12.7	3.7	15.5	6.5	17.6	8.6
	$r_{21}$	0.07	0.07	0.00	0.06	0.01	(12.6)	(3.6)
MMA/VDC	$r_{12}$	2.2	2.46	0.26	3.31	1.11	0.04	0.03
	$r_{21}$	0.28	0.41	0.13	0.30	0.02	(0.05)	(0.02)
MA/B	$r_{12}$	0.07	0.13	0.06	0.07	0.00	0.18	0.11
	$r_{21}$	1.09	2.14	1.05	1.01	0.08	0.60	0.49
MA/I	$r_{12}$	0.12	0.11	0.01	0.04	0.08	0.11	0.01
	$r_{21}$	0.75	2.30	1.55	0.86	0.11	0.92	0.17
MA/MAN	$r_{12}$	0.50	0.54	0.04	0.43	0.07	0.51	0.01
	$r_{21}$	2.00	1.86	0.14	2.25	0.25	2.69	0.69
MA/VA	$r_{12}$	6.50	6.54	0.04	9.88	3.38	15.0	8.5
	$r_{21}$	0.03	0.02	0.01	0.05	0.02	(9.3)	(2.8)
MA/VC	$r_{12}$	6.00	5.91	0.09	7.51	1.51	0.09	0.06
	$r_{21}$	0.09	0.13	0.04	0.11	0.02	(0.07)	(0.04)
MA/VDC	$r_{12}$	0.92	1.20	0.28	1.86	0.94	8.21	2.21
	$r_{21}$	0.80	0.76	0.04	0.57	0.23	(5.98)	(0.02)
MAN/B	$r_{12}$	0.05	0.23	0.18	0.10	0.05	0.08	0.01
	$r_{21}$	0.39	1.10	0.71	0.30	0.09	(0.13)	(0.04)
MAN/I	$r_{12}$		0.19		0.06		1.20	0.28
	$r_{21}$		1.18		0.25		0.54	0.26

## ARTICLE

MAN/VA	$r_{12}$	12.0	11.5	0.5	18.7	6.70	27.8	15.8
	$r_{21}$	0.01	0.01	0.00	0.02	0.01	(17.6)	(5.6)
MAN/VC	$r_{12}$		10.8		15.5		15.4	
	$r_{21}$		0.07		0.04		(11.3)	(0.02)
MAN/VDC	$r_{12}$	2.40	2.20	0.20	3.54	1.14	2.29	0.11
	$r_{21}$	0.33	0.40	0.07	0.23	0.10	0.21	0.12
2CB/2VP	$r_{12}$	5.19	1.07	4.12	5.64	0.45	4.71	0.48
	$r_{21}$	0.06	0.07	0.01	0.14	0.08	0.04	0.02
MAE0 <sup>b</sup>				1.59		1.96		3.79
MAE1				0.89		0.87		0.22
MAE2								1.57

<sup>a</sup>For the monomer abbreviations, please refer to Table 1. The values represented in italics and in parentheses correspond to those calculated using the different reference reactivity ratios for VA and VC, as indicated in Table 1.

<sup>b</sup>MAE0 corresponds to the MAE for the total monomer pairs, MAE1 corresponds to the MAE for the monomers with the exception of the  $r_{12}$  values for VA and VC as monomer 2, and MAE2 corresponds to the MAE0 value calculated using different reference reactivity ratios for VA and VC.

## Discussion on the representation of the $Q$ - $e$ schemes in terms of the transition state theory

The representation of the generalized  $Q$ - $e$  schemes used in the derivation is discussed based on the transition state theory. Alfrey and Price<sup>1</sup> assumed that for the derivation of their scheme, the activation energy term of the rate constant,  $k_{12}$ , for the propagation reaction between radical 1 and monomer 2 can be partitioned into its individual contributions:

$$k_{12} = A_{12} \exp[-(p_1 + q_2 + e_1 e_2)], \quad (49)$$

where  $A_{12}$  is the frequency factor,  $p_1$  is an activation factor related to the general reactivity of radical 1,  $q_2$  is a similar factor related to the general monomer reactivity, and  $e_1$  and  $e_2$  are the electrical factors. They considered  $A_{12}$  to be essentially constant, and rewrote Equation (49) as follows:

$$k_{12} = P_{R(1)} Q_{M(2)} \exp(-e_{R(1)} e_{M(2)}), \quad (50)$$

where  $P_{R(1)}$  is the characteristic of radical 1,  $Q_{M(2)}$  is the mean reactivity of monomer 2,  $e_{R(1)}$  is proportional to the charge on the end group of radical 1, and  $e_{M(2)}$  is proportional to the charge on the double bond of monomer 2. When this relationship is applied to  $k_{11}$ ,  $k_{21}$ , and  $k_{22}$  to express the reactivity ratio of radical copolymerization, the constant  $P$  cancels out, and Equations (1) and (2) are obtained. However, Imoto<sup>26</sup> noted that Equation (50) is not valid in the case of homopolymerization because  $k_{11}$  and/or  $k_{22}$  generally

decrease with an increase in the resonance effect of the monomer (i.e., the  $Q$  value), and thus  $k_{11}$  or  $k_{22}$  must be inversely proportional to the  $Q$  value.

In contrast, the generalized  $Q$ - $e$  schemes, (11) and (12), cannot be derived from Equation (50) because the  $P_{R(1)}$  value corresponding to  $Q_{R_1}$  cancels out. Rather, it should be derived from partitioning the activation free energy difference. According to the transition state theory, the reactivity ratios are expressed as:

$$r_{12} = k_{11}/k_{12} = \exp \left[ - \left( \Delta G_{R(1)M(1)}^\ddagger - \Delta G_{R(1)M(2)}^\ddagger \right) / RT \right], \quad (51)$$

where  $\Delta G_{R(1)M(1)}^\ddagger$ ,  $\Delta G_{R(1)M(2)}^\ddagger$  are the activation free energies of  $k_{11}$ , and  $k_{12}$ , respectively. Here, we assume that the activation free energy difference (in  $RT$  units) can be partitioned in terms of the radical-specific value,  $q_{R(1)}$ ; the monomer-specific value,  $q_{M(2)}$ ; and the cross terms between radical 1 and monomers 1 and 2,  $e_{R(1)M(1)}$  and  $e_{R(1)M(2)}$  as follows:

$$\begin{aligned} & - \left( \Delta G_{R(1)M(1)}^\ddagger - \Delta G_{R(1)M(2)}^\ddagger \right) / RT \\ & \cong - (q_{R(1)} - q_{M(2)}) - (e_{R(1)M(1)} - e_{R(1)M(2)}). \end{aligned} \quad (52)$$

Here, we introduce the following terms:

$$Q_{R(1)} = \exp(-q_{R(1)}), \quad (53)$$

$$Q_{M(2)} = \exp(-q_{M(2)}). \quad (54)$$

In addition, the cross terms are approximated by the product of each  $e$  value as follows:

$$e_{R(1)M(1)} - e_{R(1)M(2)} \cong e_{R(1)}(e_{M(1)} - e_{M(2)}). \quad (55)$$

This results in Equation (11). The same holds true for Equation (12). In the Alfrey-Price  $Q$ - $e$  scheme, the following holds true between the conjugate monomer and radical 1 in the generalized  $Q$ - $e$  scheme:

$$q_{R(1)} = q_{M(1)}, \quad (56)$$

$$e_{R(1)} = e_{M(1)}. \quad (57)$$

The same applies to the conjugate monomer and radical 2. Therefore, since the assumption in Equation (50) does not hold for  $k_{11}$  and  $k_{22}$ , it is more reasonable to assume that it follows from partitioning of the reactivity ratio, i.e., partitioning of the free energy difference, rather than the rate constant. Expressions such as the intrinsic  $Q$ - $e$  scheme together with the revised patterns scheme can accurately describe the reactivity ratios (as stated for the  $Q$ - $e$  scheme, the  $Q$ - $e$ - $e^*$  scheme, the patterns scheme, and the Hammett relationship<sup>8</sup>) since the linear free-energy relationship can be generally established in the radical copolymerization reactions.

### Application to Transfer Agents

Since the intrinsic  $Q$ - $e$  scheme is equivalent to the revised patterns scheme, various approaches suggested by Jenkins<sup>27</sup> can be directly applied to it. For example, the  $Q$ - $e$  parameter can be obtained for chain transfer agents via the intrinsic  $Q$ - $e$  scheme. The transfer constant can be expressed as  $(C_2)_1 = k_{12}/k_{11}$ , where the monomer is subscripted as 1 and the transfer agent is subscripted as 2. Since this corresponds to the reciprocal of the reactivity ratio  $r_{12}$ , it can be expressed by the intrinsic  $Q$ - $e$  scheme as follows:

$$\begin{aligned} (C_2)_1 &= (Q_{M(2)}^\circ/Q_{R(1)}^\circ) \exp\{e_{R(1)}^\circ e_{M(2)}^\circ / \ln(r_{AS}r_{SA})\} \\ &= ((C_2)_S / r_{1S}) \\ &\times \exp\{\ln(r_{1A}/r_{1S}r_{SA}) \ln[(C_2)_S / (C_2)_A r_{AS}] / \ln(r_{AS}r_{SA})\}, \quad (58) \end{aligned}$$

where the intrinsic parameters in the equation are given as follows:

$$Q_{R(1)}^\circ = r_{1S}, \quad (59)$$

$$Q_{M(2)}^\circ = (C_2)_S, \quad (60)$$

$$e_{R(1)}^\circ = \ln(r_{1A}/r_{1S}r_{SA}), \quad (61)$$

$$e_{M(2)}^\circ = \ln[(C_2)_S / (C_2)_A r_{AS}]. \quad (62)$$

Thus, the transfer constants can be determined if the transfer constants of styrene and acrylonitrile ( $(C_2)_S$  and  $(C_2)_A$ , respectively) and the reactivity ratios of monomer 1 of styrene and acrylonitrile ( $r_{1S}$  and  $r_{1A}$ , respectively) are known. The  $Q$ - $e$  value is no longer required to predict the transfer constant itself, similar to the case of the reactivity ratio. However, the  $Q$ - $e$  value of the transfer agent can be obtained in the same manner as that for the  $Q$ - $e$  value of the monomer (see above) using the following equations:

$$Q_{M(2)} = Q_{R(S)} (C_2)_S \exp(e_{R(S)}^\circ \delta_{M(2)}^\circ / \delta_{R(A)}), \quad (63)$$

$$e_{M(2)} = e_{M(S)} + (\delta_{M(2)}^\circ / \delta_{R(A)}). \quad (64)$$

**Table 4** summarizes the intrinsic parameters and  $Q$ - $e$  values of the selected 15 transfer agents calculated using these equations, wherein the  $(C_2)_S$  and  $(C_2)_A$  values were taken from the *Polymer Handbook*.<sup>14</sup> The full list of the 73 calculated transfer agents is provided in Table S3. For comparison, the  $Q$ - $e$  values reported by Greenley<sup>6</sup> are also specified in the table. Unfortunately, the agreement between the calculated  $Q$ - $e$  values and those reported by Greenley is not always good, which may be because the order of magnitude for the transfer constants varies significantly among the transfer agents, and it may depend on the accuracy of the transfer constants used with styrene and acrylonitrile. Note that the reference monomer does not necessarily have to be styrene or acrylonitrile, similar to the case of reactivity ratio.

**Table 4.** Intrinsic  $Q$ - $e$  parameters ( $Q_M^\circ$ ,  $e_M^\circ$ ),  $Q$ - $e$  parameters ( $Q_M$ ,  $e_M$ ), and Greenley's  $Q$ - $e$  parameters ( $Q_G$ ,  $e_G$ ) for the transfer agents<sup>a</sup>

Transfer agent	$Q_M^\circ \times 10^4$	$e_M^\circ$	$Q_M \times 10^4$	$e_M$	$Q_G \times 10^4$	$e_G$
Acetone	0.32	1.96	0.70	0.16	0.11	0.35
Benzene	0.03	-1.19	0.23	-1.39	0.05	-1.21
Chlorobenzene	0.41	2.56	0.70	0.46	0.07	0.08
Ethylbenzene	0.7	-0.71	4.36	-1.15	0.95	-1.02
Butyl alcohol	1.6	0.95	5.16	-0.33	0.53	-0.57
Cyclohexane	0.05	-0.50	0.29	-1.05	0.11	-0.64
1,2-Dichloroethane	2	3.53	2.34	0.94	0.62	1.34
Ethyl acetate	15.5	5.03	10.0	1.68	0.07	-0.87
Dichloromethane	0.15	0.20	0.65	-0.70	0.1	-0.68
Tetrabromomethane	22000	6.47	8070	2.39	7300	2.9
Tetrachloromethane	100	7.83	21.4	3.06	3.64	3.21
Nitromethane,	10	3.73	10.8	1.04	3.26	-1.5
Methanol	0.74	3.61	0.84	0.98	0.18	-0.93
Toluene	0.12	-0.06	0.58	-0.83		
Triethylamine	7.1	-2.84	102	-2.20	28.8	-2.39

<sup>a</sup>Greenley's  $Q$ - $e$  parameters were taken from the *Polymer Handbook*.<sup>6</sup>

## ARTICLE

## Conclusions

In this study, the intrinsic  $Q-e$  scheme was derived by applying two reference monomers to the generalized  $Q-e$  scheme, which is an extension of the  $Q-e$  scheme. The derived intrinsic  $Q-e$  scheme is equivalent to the revised patterns scheme, and the intrinsic  $Q-e$  scheme together with the revised patterns scheme eliminates the arbitrariness involved in determining the parameter values, which is distinct from the original  $Q-e$  scheme. Moreover, in comparison with the  $Q-e$  scheme, their quantitative prediction of the reactivity ratios is significantly better, with the exception of the qualitative prediction for unconjugated monomers. These results indicate that the intrinsic  $Q-e$  scheme and the revised patterns scheme appear to be the most suitable approaches to non-arbitrarily and quantitatively predict the reactivity ratios within the framework of the terminal model, although it is currently unclear what effects the steric and penultimate units may impart. Furthermore, we used the intrinsic  $Q-e$  parameters to successfully determine the  $Q-e$  values of an individual monomer and radical for the first time. Although the parameters are no longer required to predict the reactivity ratios, the monomer and radical  $Q-e$  values will likely be useful for understanding the properties of these species and for their future design. The reactivity ratios can be predicted theoretically when the activation energy difference is calculated by determining the transition state of the model radical addition reactions by density functional theory (DFT) calculations. Furthermore, the  $Q-e$  or intrinsic  $Q-e$  values are suitable for developing descriptors of the monomers and radicals for materials informatics. Investigating these parameters using DFT calculations is currently in progress. In addition, since the intrinsic  $Q-e$  scheme can be applied to chain transfer agents, it is apparent that if the chain transfer constants of the two reference components, such as styrene and acrylonitrile, of the reversible addition fragmentation chain transfer agent are known, both the  $Q-e$  value and the chain transfer constant can be calculated for the polymer radical. The intrinsic  $Q-e$  scheme is expected to be applied to reversible deactivation radical polymerization in the future.

## Author contributions

Susumu Kawauchi: conceptualization, data curation, formal analysis, investigation, methodology, resources, supervision, validation, visualization, writing – original draft. Akinori Akatsuka: data curation, formal analysis, writing – review and editing. Yoshihiro Hayashi: writing – review and editing.

Hidemine Furuya: writing – review and editing. Toshikazu Takata: funding acquisition, project administration, writing – review and editing.

## Conflicts of interest

There are no conflicts to declare.

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