A Consideration of the Q-e Scheme. IV. A Theoretical Approach to Price-Alfrey's Polarity Term

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Part I of this series[1] described a revised pattern of Price-Alfrey's *Q-e* scheme[2] which assumed the *e*-value of styrene to be equal to zero. In Part II,[3] we tried to give some theoretical background for this scheme. We divided the conjugation-stabilization energy between the monomer and the attacking radical, E_{RM}, into four terms by means of the following equation:

$$E_{RM} = E_{RoMo} + E_R + E_M + E'_{RM} \quad (1)$$

Here, E_{RoMo} is the stabilization energy between the polyethylene radical and the ethylene monomer, and E_R and E_M are the increments in the stabilization energy over E_{RoMo} as the standard introduced by the substituents in the polymer radical and in the monomer molecule respectively. E'_{RM} is the surplus increment in the stabilization energy introduced by the substituents of the radical and the monomer. We proposed relations 2 to 4 for the *P*-, *Q*- and *e*-terms:

$$P \propto \exp(E_R/\boldsymbol{RT}) \quad (2)$$

$$\ln Q_1 - \ln Q_2 = (E_{M_1} - E_{M_2})/\boldsymbol{RT} \quad (3)$$

$$e_R e_M = -E'_{RM}/\boldsymbol{RT} \quad (4)$$

The classical interpretation of the *P*-, *Q*- and *e*-terms is obviously different from ours, especially in the explanation of the polarity term. According to the classical interpretation,[2b] *e* is proportional to the charge on the end group of the radical or the monomer. Both of the two interpretations correlate with experimental facts; therefore, some theoretical interrelation may exist between them. The electronic charge on the end group of the radical or the monomer seems to be introduced mainly by heteroatoms. Therefore, we tried to investigate the effect of heteroatoms on the *Q-e* terms.

1) N. Kawabata, T. Tsuruta and J. Furukawa, *Makromol. Chem.*, **51**, 70 (1962).
2) a) T. Alfrey, Jr., and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947). b) T. Alfrey, Jr., J. J. Bohrer and H. Mark, "Copolymerization," Interscience Publisher, New York (1952).
3) N. Kawabata, T. Tsuruta and J. Furukawa, *Makromol. Chem.*, **51**, 80 (1962).

The Effect of Heteroatoms on the Conjugation-stabilization Energy. — In Part II of this series,[3] we proposed relations 2—4 for the *P*-, *Q*- and *e*-terms. Therefore, we would like now to investigate the effect of heteroatoms on the stabilization energy in order to examine their effect on the *Q-e* terms.

The conjugation-stabilization energy, E_{RM}, was calculated by the following equation.[3-5]

$$E_{RM}=2\left(\sum_{i}^{occ}\sum_{j}^{unocc}-\sum_{j}^{occ}\sum_{i}^{unocc}\right)\frac{(C_r^j)^2(C_m^i)^2}{E_j-E_i}(\Delta\beta)^2 + \left(\sum_{i}^{occ}-\sum_{i}^{unocc}\right)\frac{(C_r^h)^2(C_m^i)^2}{E_h-E_i}(\Delta\beta)^2 \quad (5)$$

where C_r^j and C_m^i are the coefficients of the rth and the mth atomic π-orbitals in the jth and the ith molecular orbitals belonging to the eigenvalues E_j and E_i in the radical and the monomer respectively. E_h and C_r^h are the energy of the half-occupied orbital of the radical and the coefficient of the rth π-orbital in this MO respectively. $\sum^{occ}$ and $\sum^{unocc}$ imply summation over all the occupied (except the half-occupied) and all the unoccupied molecular orbitals. When the r'th atom of the radical and the m'th atom of the monomer are replaced with the heteroatoms Y and X respectively, E_j, E_i, $(C_r^j)^2$ and $(C_m^i)^2$ will become,[6] respectively:

$$E_i+\delta E_i=E_i+(C_m^i)^2\delta X \quad (6)$$

$$E_j+\delta E_j=E_j+(C_{r'}^j)^2\delta Y \quad (7)$$

$$(C_m^i)^2+\delta(C_m^i)^2=(C_m^i)^2 + 2C_m^iC_{m'}^i\sum_{p\neq i}\frac{C_m^pC_{m'}^p}{E_i-E_p}\delta X+\lambda_m(\delta X)^2 \quad (8)^*$$

$$(C_r^j)^2+\delta(C_r^j)^2=(C_r^j)^2 + 2C_r^jC_{r'}^j\sum_{q\neq j}\frac{C_r^qC_{r'}^q}{E_j-E_q}\delta Y+\lambda_r(\delta Y)^2 \quad (9)^*$$

where δX and δY are the respective increments of the Coulomb integrals for the heteroatoms X and Y. E_{RM} then becomes

$$E_{RM}=2\left(\sum_{i}^{occ}\sum_{j}^{unocc}-\sum_{j}^{occ}\sum_{i}^{unocc}\right)\times\frac{\{(C_m^i)^2+\delta(C_m^i)^2\}\{(C_r^j)^2+\delta(C_r^j)^2\}}{(E_j+\delta E_j)-(E_i+\delta E_i)}(\Delta\beta)^2 + \left(\sum_{i}^{occ}-\sum_{i}^{unocc}\right)\times\frac{\{(C_m^i)^2+\delta(C_m^i)^2\}\{(C_r^h)^2+\delta(C_r^h)^2\}}{(E_h+\delta E_h)-(E_i+\delta E_i)}(\Delta\beta)^2 \quad (10)$$

Therefore, when, by the use of Eq. 11, we separate the stabilization energy into four terms in order to investigate the effect of the heteroatoms, the E_r, E_m and E'_{rm} terms can be given by Eqs. 12—14.[7] Here, E_r and E_m are the increments in the stabilization energy introduced by the heteroatom of radical Y and by that of monomer X respectively. E'_{rm} is the surplus increment in the stabilization energy introduced by the heteroatoms of the radical and the monomer.

$$E_{RM}=E_{r_0m_0}+E_r+E_m+E'_{rm} \quad (11)$$

$$E_r=C_r(\delta Y)^2 \quad (12)^*$$

$$E_m=C_m(\delta X)^2 \quad (13)^*$$

$$E'_{rm}=-C'_{rm}(\delta X)(\delta Y) \quad (14)$$

C_m, C_r and C'_{rm} are positive constants characteristic of a series of monomers having a same skeletal structure, in which only the r'th atom of the radical and the m'th atom of the monomer are replaced by various heteroatoms.

A Theoretical Approach to Price-Alfrey's Polarity Term. — In Part II of this series,[3] we proposed relations 2—4. According to Price and Alfrey,[2] the rate constant of the propagation step, k_p, is expressed by:

$$k_p=PQ\exp(-e_Re_M) \quad (15)$$

Here, the polarity term is the product of e_R and e_M. Further, $e_{R_i}=e_{M_1}$ is assumed for the radical and the monomer of type 1. In these two points, Eq. 4 does not conform to the concept of Price and Alfrey. However, for each series of isoelectronic monomers having a same skeletal structure, in which a fixed

* $\lambda_m=(C_{m'}^i)^2\left(\sum_{p\neq i}\frac{C_m^pC_{m'}^p}{E_i-E_p}\right)^2 + 2C_m^iC_{m'}^i\sum_{l\neq i}\sum_{p\neq i}\frac{C_m^lC_{m'}^l(C_{m'}^p)^2}{(E_i-E_l)(E_i-E_p)} - 2C_m^i(C_{m'}^i)^3\sum_{l\neq i}\frac{C_m^lC_{m'}^l}{(E_i-E_l)^2}$

$\lambda_r=(C_{r'}^j)^2\left(\sum_{q\neq j}\frac{C_r^qC_{r'}^q}{E_j-E_q}\right)^2 + 2C_r^jC_{r'}^j\sum_{n\neq j}\sum_{q\neq j}\frac{C_r^nC_{r'}^n(C_{r'}^q)^2}{(E_j-E_n)(E_j-E_q)} - 2C_r^j(C_{r'}^j)^3\sum_{n\neq j}\frac{C_r^nC_{r'}^n}{(E_j-E_n)^2}$

* When the reference monomer and the reference radical are alternant hydrocarbons, the 1st order terms cancel after summation. Therefore, Eqs. 12 and 13 are free from 1st order terms. When the reference monomer or the reference radical is a non-alternant hydrocarbon, Eqs. 12 and 13 may not be correct, although such a case is of rare occurrence.

4) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3341 (1952).
5) T. Yonezawa, K. Hayashi, C. Nagata, S. Okamura and K. Fukui, *J. Polymer Sci.*, **14**, 312 (1954); K. Hayashi, T. Yonezawa, C. Nagata, S. Okamura and K. Fukui, ibid., **20**, 537 (1956).
6) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39 (1947).
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TABLE I. REVISED *Q*-*e* VALUES

Vinyl compound	*e*	*Q*
Vinylidene cyanide	3.5	200
Methyl α-phenylacrylate[9]	2.8	21
N-Vinylpyridinium-fluoroborate[10]	2.4	3.6
Di-β-chloroethyl itaconate	2.3	3.0
Methyl α-chloroacrylate	2.0	9
1,1-Dihydroperfluorobutyl acrylate	2.0	3.0
Chloroprene	2.0	2.0
p-Potassium styrenesulfonate	1.9	5.5
Acrylamide	1.9	3.0
Acrylonitrile	1.9	2.7
α-Acetoxyacrylonitrile	1.8	5
N-Benzylidene-4-methacryloxy-aniline	1.8	4
α, β, β-Trifluorostyrene	1.8	1.5
Methacrylonitrile	1.7	3.3
Dibutyl itaconate	1.6	3.8
Itaconic acid	1.6	3.3
Dimethy itaconate	1.6	2.1
n-Butyl vinyl sulfonate	1.6	0.4
Acrylic acid	1.6	0.4
N,*N*,*N*-Triethyl-*N*-(2-methacryloxy-ethyl)-ammonium iodide	1.5	4
Methyl vinyl ketone	1.5	3.5
Methacrylic acid	1.5	3.0
Acrolein	1.5	1.6
n-Octyl acrylate	1.5	1.5
Butyl acrylate	1.5	1.3
Abietyl acrylate	1.5	1.3
Methyl vinyl sulfone	1.5	0.5
Phenyl vinyl sulfone	1.5	0.3
Methyl thiolacrylate	1.4	3.0
Methyl acrylate	1.4	1.3
Pentachlorostyrene	1.4	0.8
Chlorotrifluoroethylene	1.4	0.14
Vinyl perfluorobutyrate	1.4	0.1
Tetrafluoroethylene	1.4	0.07
2,3-Dichloro-1,3-butadiene	1.3	25
4-Vinylpyrimidine	1.3	6
Stearyl methacrylate	1.3	1.9
β-Chloroethyl acrylate	1.3	1.8
Hydronopyl acrylate	1.3	1.5
Vinyl trifluoroacetate	1.3	0.03
p-Nitrostyrene	1.2	5.3
p-Sulfonamidostyrene	1.2	4.3
Methyl isopropenyl ketone	1.2	3.0
Ethyleneglycol dimethacrylate	1.2	2.9
Methacrolein	1.2	2.3
Decyl methacrylate	1.2	2.0
Methyl methacrylate	1.2	1.9
Ethyl methacrylylaminoacetate	1.2	1.8
Nonyl methacrylate	1.2	1.7
Ethyl methacrylate	1.2	1.5
Vinyl fluoride	1.2	0.09
p-Cyanostyrene	1.1	3.6
2-Vinylpyridine	1.1	1.8
Vinylidene chloride	1.1	0.5
2-Chloroallyl alcohol	1.1	0.08
m-Nitrostyrene	1.0	2.2
4-Vinylpyridine	1.0	1.7
n-Butyl methacrylate	1.0	1.5
Vinyl isothiocyanate	1.0	1.3
Ethyl acrylate	1.0	1.3
Allyl alcohol	1.0	0.15
2-(*N*,*N*-Dimethylamino)-4-vinylpyrimidine	0.9	2.9
Methacryloxymethylpentamethyl-disiloxane	0.9	1.3
Isobutyl methacrylate	0.9	1.2
2-Chloroallyl chloride	0.9	0.2
Allyl chloride	0.9	0.03
n-Octyl methacrylate	0.8	2.9
2,5-Bis(trifluoromethyl)styrene	0.8	2.2
Glycidyl methacrylate	0.8	1.5
n-Hexyl methacrylate	0.8	1.0
Methacrylamide	0.8	0.7
4-Methacryloxybenzylideneaniline	0.7	4.0
2-Fluoro-1,3-butadiene	0.7	2.0
m-Bromostyrene	0.7	1.8
Isopropenyl methacrylate	0.7	1.5
Allyl laurate	0.7	0.03
6-Chloro-2-vinylnaphthalene	0.6	2.5
m-Chlorostyrene	0.6	1.6
p-Iodostyrene	0.6	1.6
p-Chlorostyrene	0.6	1.4
p-Bromostyrene	0.6	1.4
N-(1,1-Dihydroperfluorobutyl)-*N*-ethyl acrylamide	0.6	1.2
4-Chloro-1-vinylnaphthalene	0.6	1.2
n-Amyl methacrylate	0.6	0.9
N-Vinylsuccinimide	0.6	0.14
Dimethallyl oxalate	0.6	0.06
Diallyl phthalate	0.6	0.03
4-Methacryloxybenzilidene-4'-chloroaniline	0.5	6
n-Propyl methacrylate	0.5	1.5
3-Trifluoromethylstylene	0.5	1.4
t-Butyl methacrylate	0.5	1.3
Isopropenylacetylene	0.5	0.6
4,6-Diamino-2-vinyl-*s*-triazine	0.4	2.6
Vinyl chloride	0.4	0.06
Sodium styrenesulfonate	0.3	2.6
o-Chlorostyrene	0.3	1.8
2-Methyl-5-vinylpyridine	0.3	1.3
Vinyl bromide	0.3	0.05
5-Ethyl-2-vinylpyridine	0.2	1.3
N-Methyl methacrylamide	0.2	0.4
Pentachlorophenyl vinyl sulfide	0.2	0.25
Vinyl isocyanate	0.2	0.13
Vinyl palmitate	0.2	0.02
Vinyl caprate	0.2	0.01
Vinyl dichloroacetate	0.1	0.05
2-Vinylphenanthrene	0.0	4

TABLE I. continued.

Vinyl compound	*e*	*Q*
3-Vinylphenanthrene	0.0	4
2-Vinylthiophene	0.0	2.9
2-Vinylquinoline	0.0	2.0
2-Vinylnaphthalene	0.0	2.0
Vinylacetylene	0.0	1.6
1-Vinylnaphthalene	0.0	1.5
p-Trimethoxysilylstyrene	0.0	1.4
N-(*p*-Tolyl) methacrylamide	0.0	1.3
1,3-Butadiene	0.0	1.3
α-Acetoxystyrene	0.0	1.1
m-Vinylphenol	0.0	1.1
m-Methylstyrene	0.0	1.0
Styrene	(0.0)	(1.00)
p-Trimethylsilylstyrene	0.0	1.0
o-Methylstyrene	0.0	0.9
N-Phenyl methacrylamide	0.0	0.9
Phenylacetylene	0.0	0.7
N-Ethyl methacrylamide	0.0	0.3
Isopropenyl isocyanate	0.0	0.14
Vinyl ethyl oxalate[11]	0.0	0.12
Vinyl formate	0.0	0.10
Vinyl chloroacetate	0.0	0.05
Vinyl butyrate	0.0	0.03
Vinyl propionate	0.0	0.03
Vinyl benzoate	0.0	0.03
Vinyl undecylenate	0.0	0.03
Vinyl pelargonate	0.0	0.03
N-Vinyl-2-oxazolidinone	0.0	0.03
Vinyl acetate	0.0	0.02
Tris(trimethylsiloxyl) vinylsilane	0.0	0.02
Vinyl laurate	0.0	0.01
Ethylene	0.0	0.01
Allyl acetate	0.0	0.01
2-Vinylmercaptobenzothiazole	−0.1	1.5
2,5-Dimethylstyrene	−0.1	1.0
p-Methylstyrene	−0.1	0.9
N-(*p*-Chlorophenyl) methacrylamide	−0.1	0.7
Ethyl vinyl sulfide	−0.1	0.2
Vinyl levulinate	−0.1	0.02
Bis(trimethylsiloxyl) vinylmethylsilane	−0.1	0.02
p-Acetylaminostyrene	−0.2	1.3
β-Isopropenylnaphthalene	−0.2	0.9
p-Methoxystyrene	−0.2	0.9
Divinyl sulfide	−0.2	0.5
N-Methyl-*N*-vinyl-*p*-toluenesulfonamide	−0.2	0.08
N-Vinylpyrrolidone	−0.2	0.08
Isopropenyl acetate	−0.2	0.03
Vinyl isocaproate	−0.2	0.03
Vinyl caprylate	−0.2	0.02
Vinyl pinonate	−0.2	0.02
Vinyl stearate	−0.2	0.02
Vinyl caproate	−0.2	0.02
Isoprene	−0.3	2.0
α-Methylstyrene	−0.3	1.1
N-(*p*-Anisyl) methacrylamide	−0.3	0.25
p-Dimethylaminostyrene	−0.4	1.0
Phenyl vinyl sulfide	−0.6	0.2
Isobutylene	−0.6	0.02
Methyl vinyl sulfide	−0.7	0.2
9-Vinyl carbazole	−0.9	0.2
N-Ethyl-*N'*-vinylurea	−1.1	0.05
N-Vinylurethane	−1.4	0.06
Isobutyl vinyl ether	−1.4	0.02

carbon atom of a reference monomer (ethylene, butadiene, styrene or another neutral monomer) is replaced by such a heteroatom as oxygen, nitrogen, etc., the surplus energy term, E'_{RM}, seems to satisfy the concept. For these series of monomers, Eqs. 2−4 can, respectively, be reduced to

$$P \propto \exp(E_r/\boldsymbol{RT}) \tag{16}$$

$$\ln Q - \ln Q_0 = E_m/\boldsymbol{RT} \tag{17}$$

$$e_R e_M = -E'_{rm}/\boldsymbol{RT} \tag{18}$$

Here, Q_0 is the Q-value of the reference monomer of a monomer series. From Eqs. 12, 13 and 14, Eqs. 16, 17 and 18 can, respectively, be reduced to:

$$P \propto \exp\{(C_r/\boldsymbol{RT})(\delta Y)^2\} \tag{19}$$

$$\ln Q - \ln Q_0 = (C_m/\boldsymbol{RT})(\delta X)^2 \tag{20}$$

$$e_R e_M = (C'_{rm}/\boldsymbol{RT})(\delta X)(\delta Y) \tag{21}$$

Here, C_r, C_m and C'_{rm} are constants characteristic of a series of monomers having a same skeletal structure. As can be seen in Eq. 21, the polarity term may reasonably be separated into two terms, e_R and e_M, for such a monomer series.

$$e_R = -\sqrt{C'_{rm}/\boldsymbol{RT}}(\delta Y) \tag{22}$$

$$e_M = -\sqrt{C'_{rm}/\boldsymbol{RT}}(\delta X) \tag{23}$$

The assumption by Price and Alfrey that $e_{R_1} = e_{M_1}$ for the radical and the monomer of type 1 also seems to be reasonable for a monomer series of the same skeletal type.

Revised *Q-e* Values. — On the basis of the copolymerization data collected by Young,[8] we calculated the revised *Q-e* values by assuming the *e*-value of styrene to be equal to zero. These values are given in Table I.

We also calculated the $e_R e_M$ values as the

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9) K. Chikanishi, unpublished finding.
10) Irl. N. Duling and C. C. Price, *J. Am. Chem. Soc.*, **84**, 578 (1962).
11) N. Kawabata, T. Tsuruta and J. Furukawa, *Makromol. Chem.*, **48**, 106 (1961).

products of the relevant e-values given in Table I. These $e_R e_M$ values were compared with the e_{RM} values.[1] For each series of isoelectronic monomers having a same skeletal structure, the average deviation of $e_R e_M$ from e_{RM} was about 7%. However, for other pairs of radical and monomer, the average error was nearly 35%. This finding shows the validity of our conclusion that the expression by Price and Alfrey is reasonable for a series of monomers having a same skeletal structure.

An Electrostatic Interpretation of the Polarity Term.—According to the classical interpretation,[2b] e is proportional to the charge on the end group of the radical or the monomer. In fact, a linear relation was observed between $q_R q_M$ and $e_R e_M$.[3] That is,

$$e_R e_M \propto q_R q_M \tag{24}$$

Here, q_R and q_M are π-electronic charges on the end groups of the radical and the monomer respectively. According to Price,[12] it would be a reasonable speculation to write

$$e_R e_M = \varepsilon_R \varepsilon_M / rDkT \tag{25}$$

Here, ε_R and ε_M are actual charges on the end groups of the radical and the monomer respectively. D is the effective dielectric constant, and r is the distance of separation in the activated complex. However, there has often been proposed a different opinion that the electron transfer from a donor radical to an acceptor monomer, or vice versa, in the activated complex may account for the alternation tendency.[3,13-18] For a series of monomers having a same skeletal structure, q_R and q_M can be expressed as follows on the basis of Eqs. 8 and 9:

$$q_R = -2\sum_{j}^{occ} \delta(C_r^j)^2 e - \delta(C_r^h)^2 e = C_R(\delta Y) \tag{26}$$

$$q_M = -2\sum_{i}^{occ} \delta(C_m^i)^2 e = C_M(\delta X) \tag{27}$$

Here, C_R and C_M are negative constants characteristic of the series of monomers. From Eqs. 22 and 26,

$$e_R = -(\sqrt{C'_{rm}/\boldsymbol{RT}}/C_R) q_R \tag{28}$$

From Eqs. 23 and 27,

$$e_M = -(\sqrt{C'_{rm}/\boldsymbol{RT}}/C_M) q_M \tag{29}$$

The correlation of the polarity term with the product of π-electronic charges (Eq. 24) seems to be ascribable to the relations 28 and 29.

Summary

Previously, we pointed out the correlations of the P-, Q- and e-terms with the components of the conjugation-stabilization energy between monomers and attacking radicals. In the present paper, the effect of heteroatoms on the components of the stabilization energy was investigated. For each series of isoelectronic monomers, in which a fixed carbon atom of a reference monomer (ethylene, styrene, butadiene or another neutral monomer) is replaced by a heteroatom (oxygen, nitrogen, etc.), we obtained the relations: $\ln Q - \ln Q_0 = (C_m/\boldsymbol{RT})(\delta X)^2$, $P \propto \exp(C_r/\boldsymbol{RT})(\delta Y)^2$, $e_R = -\sqrt{C'_{rm}/\boldsymbol{RT}}(\delta Y)$ and $e_M = -\sqrt{C'_{rm}/\boldsymbol{RT}}(\delta X)$. Here, C_m, C_r and C'_{rm} are positive constants characteristic of the monomer series, while δX and δY are the Coulomb integral increments of the heteroatoms (relative to a carbon atom) in the monomer X and the radical Y respectively. Q_0 is the Q-value of the reference monomer of the series. The e-values of the reference monomers were all assumed to be zero. The opinions of Price and Alfrey that the polarity term is the product of e_R and e_M and that $e_{R_1} = e_{M_1}$ for the radical and the monomer of type 1 seem to be not only convenient but also reasonable for a series of monomers having a same skeletal structure. The π-electronic charges, q_R and q_M, on the end groups of the radical and the monomer seem to be correlated with e_R and e_M in such a manner that $e_R = -(\sqrt{C'_{rm}/\boldsymbol{RT}}/C_R) q_R$ and $e_M = -(\sqrt{C'_{rm}/\boldsymbol{RT}}/C_M) q_M$. Here, C_R and C_M are negative constants characteristic of the series of monomers. The correlation of the polarity term with the electrostatic interaction between the charges of the radical and the monomer seems to be ascribable to these relations.

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