Consideration on the Q-e Scheme. III. Q-e Factors in Ionic Polymerization

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The reactivity of vinyl compounds in radical copolymerization has been generalized by the *Q-e* scheme proposed by Alfrey and Price[1]. According to the scheme, the rate constant of propagation step, k_p, is expressed by the following equation:

$$k_p=P_R Q_M \exp(-e_R e_M) \tag{1}$$

where P is the reactivity associated with polymer radical, Q is the general reactivity term characteristic of the monomer and e is the polarity term characteristic of the radical and the monomer. In part I of this series[2], a revised pattern of the scheme by assuming the *e*-value of styrene to be equal to zero was described and a notation e_{RM} was proposed instead of $e_R e_M$ for the polarity term. In part II of this series[3], we tried to give some theoretical background to the scheme. We tried to divide the conjugation-stabilization energy between monomer and attacking radical[4], E_{RM}, into four terms by the following equation:

$$E_{RM}=E_{R_0M_0}+E_R+E_M+E'_{RM} \tag{2}$$

where $E_{R_0M_0}$ is the stabilization energy between polyethylene radical and ethylene monomer, E_R and E_M are the increments in the stabilization energy introduced by the substituent of radical and by that of monomer, respectively, $E_{R_0M_0}$ as standard. E'_{RM} is the surplus increment in the stabilization energy introduced by the substituents of the radical and the monomer. We proposed the relations 3 to 5 for *P*-, *Q*- and *e*-terms.

$$P_R \propto \exp(E_R/\boldsymbol{RT}) \tag{3}$$

$$\ln Q_1-\ln Q_2=(E_{M_1}-E_{M_2})/\boldsymbol{RT} \tag{4}$$

$$e_{RM}=-E'_{RM}/\boldsymbol{RT} \tag{5}$$

For ionic copolymerization, however, no such generalization has been established, although several attempts have been made[5]. The most characteristic feature of ionic copolymerization has long been considered to be that the product of monomer reactivity ratios, r_1r_2, is close to unity. Thus,

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[1] T. Alfrey, Jr., and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947); T. Alfrey, Jr., J. J. Bohrer and H. Mark, "Copolymerization", Interscience Publishers, New York (1952).

[2] N. Kawabata, T. Tsuruta and J. Furukawa, *Makromol. Chem.*, **51**, 70 (1962).

[3] N. Kawabata, T. Tsuruta and J. Furukawa, ibid., **51**, 80 (1962).

[4] 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); G. S. Levinson, ibid., **60**, 43 (1962).

[5] a) C. G. Overberger, L. H. Arond, D. Tanner, J. J. Taylor and T. Alfrey, Jr., *J. Am. Chem. Soc.*, **74**, 4848 (1952); b) Y. Landler, *J. Polymer Sci.*, **8**, 63 (1952); G. E. Ham, ibid., **14**, 483 (1954).

TABLE I. CONJUGATION-STABILIZATION ENERGY BETWEEN

Monomer	Styrene	Butadiene	Ethylene	Acrylonitrile	Methacrylonitrile	Vinylidene cyanide	Methyl vinyl ketone
Styrene	0.860	0.842	1.064	1.165	1.046	1.228	1.289
Butadiene	0.871	0.854	1.079	1.187	1.063	1.255	1.316
Ethylene	0.692	0.680	0.833	0.833	0.778	0.802	0.884
Acrylonitrile	0.688	0.678	0.804	0.836	0.772	0.830	0.893
Methacrylonitrile	0.735	0.722	0.874	0.912	0.838	0.907	0.980
Vinylidene cyanide	0.641	0.632	0.722	0.767	0.706	0.775	0.819
Methyl vinyl ketone	0.658	0.655	0.759	0.785	0.728	0.775	0.835
Methyl acrylate	0.692	0.681	0.815	0.837	0.776	0.823	0.893
Methyl methacrylate	0.743	0.729	0.889	0.917	0.846	0.904	0.983
Vinyl acetate	0.769	0.755	0.942	0.991	0.905	1.003	1.077
Vinyl chloride	0.778	0.765	0.952	0.986	0.907	0.907	1.066
Vinylidene chloride	0.798	0.783	0.993	1.053	0.958	1.064	1.145
α-Methylstyrene	0.916	0.896	1.148	1.266	1.131	1.348	1.409
p-Methylstyrene	0.870	0.854	1.079	1.189	1.064	1.264	1.317
p-Chlorostyrene	0.863	0.849	1.069	1.177	1.054	1.252	1.304
p-Methoxystyrene	0.973	0.952	1.230	1.680	1.361	4.401	2.174

TABLE II. CONJUGATION-STABILIZATION ENERGY BETWEEN

Monomer	Styrene	Butadiene	Ethylene	Acrylonitrile	Methacrylonitrile	Vinylidene cyanide	Methyl vinyl ketone
Styrene	0.859	0.843	1.064	0.666	0.682	0.552	0.652
Butadiene	0.871	0.854	1.079	0.672	0.688	0.556	0.657
Ethylene	0.692	0.680	0.833	0.571	0.581	0.487	0.562
Acrylonitrile	1.300	1.269	1.710	0.837	0.866	0.654	0.808
Methacrylonitrile	1.234	1.204	1.610	0.807	0.836	0.636	0.781
Vinylidene cyanide	1.866	1.817	2.534	1.042	1.091	0.776	0.996
Methyl vinyl ketone	1.372	1.339	1.816	0.864	0.895	0.670	0.833
Methyl acrylate	1.091	1.066	1.404	0.763	0.785	0.611	0.742
Methyl methacrylate	1.027	1.004	1.309	0.734	0.755	0.593	0.714
Vinyl acetate	0.718	0.705	0.867	0.588	0.599	0.493	0.577
Vinyl chloride	0.779	0.765	0.952	0.627	0.639	0.527	0.615
Vinylidene chloride	0.811	0.796	0.995	0.646	0.659	0.540	0.634
α-Methylstyrene	0.806	0.791	0.984	0.640	0.647	0.536	0.627
p-Methylstyrene	0.851	0.835	1.050	0.662	0.678	0.550	0.649
p-Chlorostyrene	0.862	0.848	1.067	0.667	0.683	0.553	0.671
p-Methoxystyrene	0.814	0.799	0.995	0.647	0.663	0.542	0.634

$$k_{11}/k_{12} \doteqdot k_{21}/k_{22} \qquad (6)$$

Here, k_{AB} is the propagation rate constant for polymer ion A and monomer B. Landler[5b] and Pepper[6] interpreted the relation 6 in terms of the nearly equal reactivities of polymer ions, i. e.,

$$k_{11} \doteqdot k_{21} \qquad (7)$$

and

$$k_{12} \doteqdot k_{22} \qquad (8)$$

However, this assumption has been denied by some experimental results of Okamura et al.[7], who showed that the polymer cation derived from a less reactive monomer had the larger reactivity. The same conclusion was reached in anionic copolymerization by Kuntz and O'Driscoll[8]. The $r_1r_2 \doteqdot 1$ relation was afforded by Okamura et al., who assumed that the rate constant of propagation reaction, k_p, was expressed as a product of the reactivity of ion R_I and that of monomer R_M, i. e.,

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[6] D. C. Pepper, *Quart. Revs.*, **8**, 88 (1954).

[7] S. Okamura, N. Kanoh and T. Higashimura, *Makromol. Chem.*, **47**, 35 (1961).

[8] K. F. O'Driscoll and I. Kuntz, *J. Polymer Sci.*, **61**, 19 (1962).

MONOMER AND ATTACKING CATION, $E_{\mathrm{CM}}(-(\Delta\beta)^2/\beta)$

Polymer cation								
Methyl acrylate	Methyl methacrylate	Vinyl acetate	Vinyl chloride	Vinyliden chloride	α-Methyl-styrene	*p*-Methyl-styrene	*p*-Chloro-styrene	*p*-Methoxy-styrene
1.178	1.050	0.885	0.991	0.927	0.807	0.852	0.860	0.781
1.200	1.067	0.896	1.005	0.940	0.816	0.862	0.867	0.789
0.855	0.793	0.716	0.781	0.734	0.661	0.687	0.690	0.646
0.848	0.777	0.708	0.763	0.724	0.652	0.684	0.687	0.669
0.927	0.846	0.761	0.824	0.779	0.696	0.732	0.734	0.702
0.772	0.705	0.657	0.695	0.667	0.606	0.639	0.642	0.653
0.796	0.733	0.677	0.724	0.690	0.625	0.656	0.658	0.649
0.853	0.784	0.713	0.771	0.731	0.658	0.688	0.691	0.680
0.935	0.856	0.765	0.836	0.788	0.704	0.737	0.741	0.701
1.009	0.916	0.793	0.858	0.810	0.727	0.762	0.760	0.703
1.009	0.917	0.805	0.890	0.835	0.738	0.773	0.777	0.719
1.071	0.967	0.835	0.928	0.870	0.764	0.803	0.807	0.743
1.282	1.136	0.944	1.064	0.992	0.858	0.906	0.912	0.821
1.200	1.067	0.895	1.004	0.939	0.816	0.861	0.867	0.788
1.188	1.057	0.888	0.995	0.931	0.810	0.854	0.860	0.784
1.576	1.300	0.993	1.139	1.061	0.897	0.962	0.968	0.854

MONOMER AND ATTACKING ANION, $E_{\mathrm{AM}}(-(\Delta\beta)^2/\beta)$

Polymer anion								
Methyl acrylate	Methyl methacrylate	Vinyl acetate	Vinyl chloride	Vinylidene chloride	α-Methyl-styrene	*p*-Methyl-stylene	*p*-Chloro-styrene	*p*-Methoxy-styrene
0.718	0.750	0.992	0.991	0.927	0.919	0.870	0.857	0.911
0.726	0.757	1.006	1.015	0.940	0.931	0.881	0.867	0.923
0.608	0.627	0.776	0.781	0.735	0.724	0.698	0.690	0.719
0.953	1.016	1.615	1.579	1.466	1.467	1.327	1.293	1.472
0.916	0.972	1.522	1.487	1.393	1.388	1.260	1.206	1.386
1.228	1.338	2.449	2.326	2.149	2.218	1.920	1.853	2.245
0.990	1.059	1.718	1.675	1.554	1.558	1.391	1.364	1.565
0.854	0.899	1.306	1.302	1.213	1.190	1.108	1.085	1.199
0.813	0.855	1.221	1.214	1.132	1.117	1.042	1.022	1.113
0.624	0.646	0.809	0.811	0.748	0.755	0.724	0.715	0.748
0.672	0.695	0.884	0.889	0.835	0.821	0.787	0.777	0.815
0.694	0.720	0.924	0.929	0.871	0.856	0.819	0.808	0.850
0.685	0.712	0.921	0.917	0.858	0.859	0.814	0.803	0.850
0.713	0.744	0.979	0.978	0.916	0.907	0.860	0.848	0.900
0.720	0.751	0.995	0.994	0.940	0.921	0.872	0.858	0.914
0.692	0.720	0.930	0.928	0.869	0.866	0.822	0.810	0.857

$$k_{\mathrm{p}} = R_{\mathrm{I}} R_{\mathrm{M}} \tag{9}$$

Recently, Szwarc et al.[9,10] have found several anionic copolymerization systems in which the reactivity ratio products determined directly by the use of living polymers are less than unity. Thus, the widely held view that $r_1 r_2$ products for ionic copolymerizations are always nearly equal to unity seems to require some amendment. The authors herewith have tried to give an interpretation of these experimental facts by a logical extention of the *Q-e* scheme for radical polymerization investigated in previous papers[2,3] to the ionic case. *P*-, *Q*- and *e*-terms were therefore regarded as corresponding to the components of the conjugation-stabilization energy between monomer and attacking ion, much as in the case of radical copolymerization[3].

Method of Calculation

On the basis of Dewar's LCAO MO second-order perturbation method[11], the conjugation-stabilization energy between the attacking

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[9] C. L. Lee, J. Smid and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 2961 (1961).

[10] J .Smid and M. Szwarc, *J. Polymer. Sci.*, **61**, 31 (1962).

[11] M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3341 (1952).

polymer ion and the monomer was calculated as the total π-electronic energy difference between the pair of interacting mesomeric systems and the addition product formed by their union. The energy parameters adopted here are those used in the preceding paper³⁾.

Results and Discussion

P-, Q- and e-Terms in Ionic Polymerization. —As has been mentioned above, we assume that the activation energy, E_p, in ionic polymerization can be expressed by Eq. 10, as in radical polymerization;

$$E_p = C + \Delta E_\sigma + \Delta E_\pi \tag{10}$$

where C is a constant, ΔE_σ is the activation energy arising from σ-electrons, and ΔE_π is that arising from π-electrons. We further assume that C and ΔE_σ in Eq. 10 are common throughout all the ion-monomer pairs. According to the view of Fukui et al.[12], ΔE_π is the stabilization energy between the monomer and the attacking polymer ion. Thus,

$$\Delta E_\pi = -E_{\mathrm{CM}} \tag{11}$$

or

$$\Delta E_\pi = -E_{\mathrm{AM}} \tag{12}$$

where E_{CM} is the stabilization energy between monomer and polymer cation and E_{AM} is that between monomer and polymer anion. The stabilization energies recalculated by us are given in Tables I and II*1.

It can be seen in Tables I and II that the relative reactivity of the monomer or the polymer ion is consistent with some experimental results except for the extraordinarily large stabilization energies of the systems of (p-methoxystyrene monomer—vinylidene cyanide, acrylonitrile and methyl vinyl ketone cations)*2.

We tried to divide the stabilization energies into four terms by the following equations in

TABLE III. $E_M{}^+$- AND E_C-VALUE

Vinyl compound	$E_M{}^+(-(\Delta\beta)^2/\beta)$	$E_C(-(\Delta\beta)^2/\beta)$
Styrene	0.231	−0.141
Butadiene	0.246	−0.153
Ethylene	0	0
Acrylonitrile	−0.029	0.000
Methacrylonitrile	0.041	−0.055
Vinylidene cyanide	−0.111	−0.031
Methyl vinyl ketone	−0.074	0.051
Methyl acrylate	−0.018	0.022
Methyl methacrylate	0.056	−0.040
Vinyl acetate	0.109	−0.116
Vinyl chloride	0.119	−0.052
Vinylidene chloride	0.160	−0.099
α-Methylstyrene	0.315	−0.172
p-Methylstyrene	0.246	−0.146
p-Chlorostyrene	0.326	−0.143
p-Methoxystyrene	0.397	−0.187
Isobutene	0.255	−0.119

TABLE IV. SURPLUS CONJUGATION-STABILIZATION ENERGY

Monomer	Styrene	Butadiene	Ethylene	Acrylo-nitrile	Methacrylo-nitrile	Vinylidene cyanide	Methyl vinyl ketone
Styrene	−0.063	−0.069	0	+0.101	+0.037	+0.195	+0.174
Butadiene	−0.067	−0.072	0	+0.108	+0.039	+0.207	+0.186
Ethylene	0	0	0	0	0	0	0
Acrylonitrile	+0.025	+0.027	0	+0.032	+0.023	+0.057	+0.038
Methacrylonitrile	+0.002	+0.001	0	+0.038	+0.019	+0.064	+0.055
Vinylidene cyanide	+0.060	+0.063	0	+0.045	+0.039	+0.064	+0.046
Methyl vinyl ketone	+0.040	+0.049	0	+0.026	+0.024	+0.047	+0.025
Methyl acrylate	+0.018	+0.019	0	+0.022	+0.016	+0.039	+0.027
Methyl methacrylate	−0.005	−0.007	0	+0.028	+0.012	+0.046	+0.040
Vinyl acetate	−0.032	−0.034	0	+0.049	+0.018	+0.092	+0.084
Vinyl chloride	−0.033	−0.034	0	+0.034	+0.010	+0.058	+0.063
Vinylidene chloride	−0.054	−0.057	0	+0.060	+0.035	+0.102	+0.101
α-Methylstyrene	−0.091	−0.099	0	+0.118	+0.231	+0.038	+0.210
p-Methylstyrene	−0.068	−0.072	0	+0.110	+0.040	+0.216	+0.187
p-Chlorostyrene	−0.065	−0.067	0	+0.108	+0.040	+0.214	+0.184
p-Methoxystyrene	−0.116	−0.120	0	+0.450	+0.186	+3.202	+0.944

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12) T. Yonezawa, T. Higashimura, K. Katagiri, K. Hayashi, S. Okamura and K. Fukui, *J. Polymer Sci.*, **26**, 311 (1957).

*1 The conjugation-stabilization energy in ionic copolymerization was calculated by Fukui and others[12]. Our recalculated values of the energy are considerably different from theirs because we used somewhat different values of parameters, the examination of which was described in the preceding paper³⁾.

*2 In theses, cases, Dewar's second-order perturbation method is inadequate because the energy difference between the lowest vacant level of the polymer cation and highest occupied level of the monomer is too small.

the manner which had been adopted in the preceding paper[3)] for radical polymerizations:

$$E_{CM}=E_{CoMo}+E_C+E_M{}^+ +E'_{CM} \qquad (13)$$

$$E_{AM}=E_{AoMo}+E_A+E_M{}^- +E'_{AM} \qquad (14)$$

Here, E_{CoMo} is the stabilization energy between polyethylene cation and ethylene monomer, E_C and $E_M{}^+$ are the increments in the stabilization energies of the systems of (substituted polyethylene cation—ethylene monomer) and (polyethylene cation—substituted ethylene monomer) with respect to E_{CoMo} as standard. E'_{CM} is the surplus increment in the stabilization energy of the system of substituted polyethylene cation and substituted ethylene monomer. E_{AoMo}, E_A, $E_M{}^-$ and E'_{AM} have the significance analogous to E_{CoMo}, E_C, $E_M{}^+$ and E'_{CM}, respectively. The values of E_C and $E_M{}^+$ are given in Table III; those of E'_{CM}, in Table IV; those of E_A and $E_M{}^-$, in Table V; and those of E'_{AM}, in Table VI.

For ionic polymerization, we propose the relations:

$$k_{CM}=P_C{}^+Q_M{}^+\exp(-e_{CM}{}^+) \qquad (15)$$

$$k_{AM}=P_A{}^-Q_M{}^-\exp(-e_{AM}{}^-) \qquad (16)$$

which are just the logical extentions of Eq. 1 to the ionic cases. The terms $Q_M{}^+$, $P_C{}^+$, $e_{CM}{}^+$, $Q_M{}^-$, $P_A{}^-$ and $e_{AM}{}^-$ will then be given by Eqs. 17 to 22, respectively:

$$\ln Q_{M_1}{}^+ -\ln Q_{M_2}{}^+ =(E_{M_1}{}^+ -E_{M_2}{}^+)/RT \qquad (17)$$

$$P_C{}^+ \propto \exp(E_C/RT) \qquad (18)$$

$$e_{CM}{}^+ =-E'_{CM}/RT \qquad (19)$$

$$\ln Q_{M_1}{}^- -\ln Q_{M_2}{}^- =(E_{M_1}{}^- -E_{M_2}{}^-)RT \qquad (20)$$

$$P_A{}^- \propto \exp(E_A/RT) \qquad (21)$$

$$e_{AM}{}^- =-E'_{AM}/RT \qquad (22)$$

The Product of Monomer Reactivity Ratios in Ionic Polymerization. — In cationic polymerization, the surplus energy term, E'_{CM}, is negligibly small for most pairs of cations and monomers, as is obvious from Table IV*3. Therefore, Eq. 15 is reduced to Eq. 23.

TABLE V. $E_M{}^-$- AND E_A-VALUES

Vinyl compound	$E_M{}^-(-(\Delta\beta)^2/\beta)$	$E_A(-(\Delta\beta)^2/\beta)$
Styrene	0.231	−0.141
Butadiene	0.246	−0.153
Ethylene	0	0
Acrylonitrile	0.877	−0.262
Methacrylonitrile	0.777	−0.252
Vinylidene cyanide	1.701	−0.346
Methyl vinyl ketone	0.983	−0.271
Methyl acrylate	0.571	−0.225
Methyl methacrylate	0.476	−0.206
Vinyl acetate	0.034	−0.057
Vinyl chloride	0.119	−0.052
Vinylidene chloride	0.162	−0.098
α-Methylstyrene	0.151	−0.109
p-Methylstyrene	0.217	−0.135
p-Chlorostyrene	0.234	−0.143
p-Methoxystyrene	0.162	−0.114

BETWEEN MONOMER AND ATTAKING CATION, $E'_{CM}(-(\Delta\beta)^2/\beta)$

Polymer cation								
Methyl acrylate	Methyl methacrylate	Vinyl acetate	Vinyl chloride	Vinylidene chloride	α-Methyl-styrene	*p*-Methyl-styrene	*p*-Chloro-styrene	*p*-Methoxy-styrene
+0.092	+0.026	−0.062	−0.021	−0.038	−0.085	−0.066	−0.061	−0.096
+0.099	+0.028	−0.066	−0.022	−0.040	−0.091	−0.071	−0.069	−0.103
0	0	0	0	0	0	0	0	0
+0.022	+0.013	+0.021	+0.011	+0.019	+0.020	+0.026	+0.026	+0.052
+0.031	+0.012	+0.004	+0.002	+0.004	−0.006	+0.004	+0.003	+0.015
+0.028	+0.023	+0.052	+0.025	+0.044	+0.056	+0.063	+0.063	+0.118
+0.015	+0.014	+0.034	+0.017	+0.030	+0.038	+0.043	+0.042	+0.077
+0.016	+0.009	+0.015	+0.008	+0.015	+0.015	+0.019	+0.019	+0.052
+0.024	+0.007	−0.007	−0.001	−0.002	−0.013	−0.006	−0.005	−0.001
+0.045	+0.013	−0.032	−0.032	−0.033	−0.043	−0.034	−0.039	−0.052
+0.035	+0.005	−0.030	−0.010	−0.018	−0.042	−0.033	−0.032	−0.046
+0.056	+0.014	−0.041	−0.013	−0.024	−0.057	−0.044	−0.043	−0.063
+0.112	+0.028	−0.087	−0.032	−0.057	−0.118	−0.096	−0.093	−0.140
+0.099	+0.028	−0.067	−0.023	−0.041	−0.090	−0.072	−0.069	−0.104
+0.097	+0.028	−0.064	−0.022	−0.039	−0.087	−0.069	−0.066	−0.098
+0.324	+0.110	−0.120	−0.039	−0.070	−0.161	−0.122	−0.119	−0.189

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*3 This seems not to be the essential feature of cationic polymerization, but to be ascribable only to the lack of a strongly electrondonating substituent[13)].

13) N. Kawabata, unpublished finding.

TABLE VI. SURPLUS CONJUGATION-STABILIZATION ENERGY

Monomer	Styrene	Butadiene	Ethylene	Acrylonitrile	Methacrylonitrile	Vinylidene cyanide	Methyl vinyl ketone
Styrene	−0.064	−0.068	0	−0.136	−0.130	−0.166	−0.141
Butadiene	−0.067	−0.072	0	−0.145	−0.139	−0.177	−0.151
Ethylene	0	0	0	0	0	0	0
Acrylonitrile	−0.269	−0.288	0	−0.611	−0.592	−0.710	−0.631
Methacrylonitrile	−0.235	−0.253	0	−0.541	−0.522	−0.628	−0.558
Vinylidene cyanide	−0.527	−0.564	0	−1.230	−1.191	−1.412	−1.267
Methyl vinyl ketone	−0.303	−0.324	0	−0.690	−0.669	−0.800	−0.712
Methyl acrylate	−0.172	−0.185	0	−0.379	−0.367	−0.447	−0.391
Methyl methacrylate	−0.142	−0.152	0	−0.313	−0.302	−0.370	−0.324
Vinyl acetate	−0.008	−0.009	0	−0.017	−0.016	−0.028	−0.019
Vinyl chloride	−0.032	−0.034	0	−0.063	−0.061	−0.079	−0.066
Vinylidene chloride	−0.043	−0.046	0	−0.087	−0.084	−0.109	−0.090
α-Methylstyrene	−0.037	−0.040	0	−0.082	−0.085	−0.102	−0.086
p-Methylstyrene	−0.058	−0.062	0	−0.126	−0.120	−0.154	−0.130
p-Chlorostyrene	−0.064	−0.066	0	−0.138	−0.132	−0.168	−0.125
p-Methoxystyrene	−0.040	−0.043	0	−0.086	−0.080	−0.107	−0.090

$$k_{CM} \fallingdotseq P_C^+ Q_M^+ \qquad (23)$$

That is, Eq. 23, which does not involve the *e*-factor, is a good approximation of Eq. 15. This result correlates with the experimental finding that $r_1 r_2 \fallingdotseq 1$ for all the cationic copolymerization systems investigated so far. Thus, the experimental finding that $r_1 r_2 \fallingdotseq 1$ seems to be ascribable to the negligible quantity of the surplus energy term. In anionic polymerization, however, the E'_{AM} term often plays a large part in the stabilization energy, E_{AM} (Table VI). Thus, the usual claim that for ionic polymerization the $r_1 r_2$-products are always very close to unity seems not to be of general validity; it seems necessary to amend the generalization to allow for the cases where E'_{AM} is relatively large. Recent experimental findings by Szwarc et al.[9,10] favor our theoretical consideration.

Relative Reactivity toward Carbonium Ions.—According to the above discussion, the relative reactivity of vinyl compounds toward carbonium ions established by Pepper[6] and by Burnett[14] is considered to correspond to the general reactivity term in cationic polymerization, Q^+. In fact, a good linear relationship holds between the logarithm of the relative reactivity and the E_M^+-value, as is shown in Fig. 1[*4].

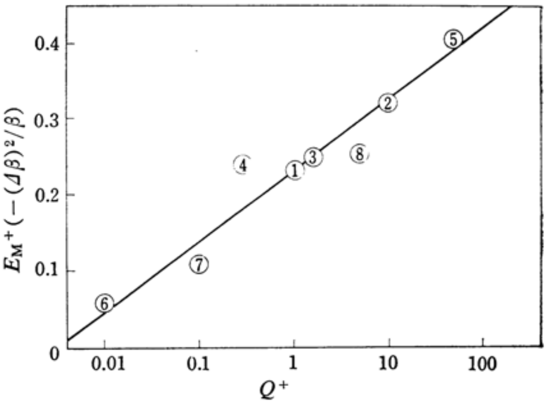

Fig. 1. Plot of E_M^+ against logarithm of Q^+.
(1) Styrene (5) *p*-Methoxystyrene
(2) *α*-Methylstyrene (6) Methyl methacrylate
(3) *p*-Methylstyrene (7) Vinyl acetate
(4) *p*-Chlorostyrene (8) Isobutene

Overberger et al.[5a] pointed out that when the logarithm of the relative reactivity of substituted styrenes toward *α*-methylstyrene carbonium ions was plotted against Hammett's substituent constant *σ*, large deviations of plots from linearity were observed in the cases of the substituents $-OCH_3$ and $-N(CH_3)_2$. Tsuruta (one of the authors) has suggested that linearity was improved when σ^+ was used instead of σ for these substituents[16]. A linear relationship was also observed between σ^+ and E_M^+.

Conclusion

The correlation of the monomer reactivity ratios in ionic polymerization with the conjugation-stabilization energy between monomer

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[14] G. M. Burnett, " Mechanism of Polymer Reactions ", Interscience Publishers, New York (1954), p. 418.

[*4] Later experimental data[15] are included here.

[15] T. Higashimura and S. Okamura, Abstracts of the 13th Meeting of Japan Chemical Society, (1960), p. 361; S. Okamura, T. Higashimura and K. Takeda, *Chem. High Polymers (Kobunshi Kagaku)*, **18**, 389 (1961); A. V. Tobolsky and R. J. Bondreau, *J. Polymer Sci.*, **51**, s 53 (1961).

[16] T. Tsuruta, *J. Japanese Chem. (Kagaku no Ryoiki)*, **8**, 209 (1954); *Bull. Inst. Chem. Research, Kyoto Univ.*, **32**, 149 (1954).

BETWEEN MONOMER AND ATTACKING ANION, $E'_{AM}(-(\Delta\beta)^2/\beta)$

Polymer anion								
Methyl acrylate	Methyl methacrylate	Vinyl acetate	Vinyl chloride	Vinylidene chloride	α-Methyl-styrene	*p*-Methyl-styrene	*p*-Chloro-styrene	*p*-Methoxy-styrene
−0.121	−0.108	−0.015	−0.021	−0.039	−0.036	−0.059	−0.064	−0.039
−0.128	−0.116	−0.016	−0.022	−0.041	−0.039	−0.063	−0.069	−0.042
0	0	0	0	0	0	0	0	0
−0.532	−0.488	−0.038	−0.079	−0.146	−0.134	−0.248	−0.274	−0.124
−0.469	−0.432	−0.031	−0.071	−0.119	−0.113	−0.125	−0.261	−0.110
−1.081	−0.990	−0.028	−0.156	−0.287	−0.207	−0.479	−0.538	−0.175
−0.601	−0.551	−0.041	−0.089	−0.164	−0.149	−0.290	−0.309	−0.137
−0.325	−0.299	−0.041	−0.050	−0.093	−0.105	−0.161	−0.176	−0.091
−0.271	−0.248	−0.031	−0.043	−0.079	−0.083	−0.132	−0.144	−0.082
−0.018	−0.015	−0.001	−0.004	−0.021	−0.003	−0.008	−0.009	−0.005
−0.055	−0.051	−0.011	−0.011	−0.019	−0.022	−0.030	−0.032	−0.023
−0.076	−0.069	−0.014	−0.014	−0.026	−0.030	−0.041	−0.044	−0.031
−0.074	−0.066	−0.006	−0.015	−0.028	−0.016	−0.035	−0.038	−0.020
−0.112	−0.100	−0.014	−0.020	−0.036	−0.036	−0.055	−0.059	−0.036
−0.122	−0.110	−0.015	−0.021	−0.039	−0.037	−0.060	−0.066	−0.039
−0.078	−0.069	−0.008	−0.015	−0.028	−0.020	−0.038	−0.041	−0.024

and polymer ions pointed out by Fukui et al.[12] has been re-examined. The reactivity ratios have been satisfactorily explained in terms of the stabilization energy. The authors have also tried to explain the experimental findings that the r_1r_2 products for all the cationic copolymerization systems so far investigated are nearly equal to unity while those for several anionic copolymerization systems are appreciably smaller than unity. The experimental finding that $r_1r_2 \doteqdot 1$ seems to be ascribable to the negligible quantity of the surplus energy term.

In the present paper, the authors have assumed an ideally ionic polymerization in which various energy terms other than the stabilization energy are common throughout all ion-monomer pairs. Ionic polymerizations are sometimes largely affected by the nature of the catalyst, the cocatalyst and the solvent as well as by other experimental conditions[17-19]. In the case of radical polymerization, the reactivity of vinyl compounds can be explained satisfactorily on the basis of the stabilization energy[3,4]. In ionic polymerization, other factors than the stabilization energy, especially the electrostatic interaction between monomer and ion, should also be taken into consideration to explain the reactivity. Other factors than the stabilization energy may then be discussed.

Summary

The authors have tried to divide the conjugation-stabilization energy between monomer and attacking polymer cation, E_{CM}, and that between monomer and attacking polymer anion, E_{AM}, into four terms by means of the equations $E_{CM}=E_{CoMo}+E_C+E_M{}^++E'_{CM}$ and $E_{AM}=E_{AoMo}+E_A+E_M{}^-+E'_{AM}$, respectively. Here, E_{CoMo} is the stabilization energy between polyethylene cation and ethylene monomer, E_C and $E_M{}^+$ are the increments in the stabilization energies of systems of (substituted polyethylene cation —ethylene monomer) and (polyethylene cation —substituted ethylene monomer) with respect to E_{CoMo} as standard. E'_{CM} is the surplus increment in the stabilization energy of the system of substituted polyethylene cation and substituted ethylene monomer. E_{AoMo}, E_A, $E_M{}^-$ and E'_{AM} have the significance analogous to E_{CoMo}, E_C, $E_M{}^+$ and E'_{CM}, respectively. The E'_{CM} values for most cation-monomer pairs have been found to be negligibly small. This result correlates with the experimental findings that the products of r_1r_2 are nearly equal to unity for all the cationic copolymerization systems investigated so far. The equation, $k_{CM}=P_C{}^+Q_M{}^+\exp(-e_{CM}{}^+)$, is assumed to be applicable to cationic polymerization, the e^+-terms being, however, negligible for any cation-monomer pair. Here, $P_C{}^+$ is the reactivity associated with polymer cation, $Q_M{}^+$ is the general reactivity term of monomer in cationic polymerization, and e^+ is the corrective term characteristic of polymer cation and monomer. On the other hand, the E'_{AM} values were often found to play a large part in E_{AM}. This result

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[17] For example, T. Tsuruta et al., "Kobunshi no Gosei", Kagaku Dojin, Kyoto (1961), p. 53.

[18] S. Okamura et al., *Chem. High Polymers* (*Kobunshi Kagaku*), **18**, 267, 333, 389, 561 (1961).

[19] A. V. Tobolsky, D. J. Keller, K. F. O'Driscoll, C. E. Rogers, *J. Polymer Sci.*, **28**, 425 (1958); K. F. O'Driscoll and A. V. Tobolsky, *J. Am. Chem. Soc.*, **81**, 205 (1959); C. G. Overberger and V. G. Kamath, ibid., **81**, 2910 (1959).

is consistent with some experimental findings by Szwarc et al. The relative reactivity value of vinyl monomers toward carbonium ions is considered to be the general reactivity term in cationic polymerization, Q^+. A good correspondence of Q^+ with $E_M{}^+$ has been observed.

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