Radical Copolymerization Behavior of Alkyl Vinyl Sulfides

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SUMMARY

In order to clarify the effects of the sulfur atom and the alkyl groups in alkyl vinyl sulfides (RVS) on their reactivities, the radical copolymerizations of eight RVS (M_2) with styrene, methyl methacrylate, and acrylonitrile (M_1) were investigated at 60°C, and the copolymerization parameters were determined. It was found that the Q and e values for RVS were estimated as 0.3 ∼ 0.5 and –1.1 ∼ –1.7, respectively, from the copolymerizations with styrene, and these values were almost unchanged, regardless of the type of alkyl group in RVS. These results indicated that the electron-sharing, 3d orbital resonance between the growing radical derived from electron-donating RVS monomer and the adjacent sulfur atom was important in the transition state of copolymerizations.

It was also found that the copolymer composition curves in the copoly-merizations of RVS varied widely with the comonomers used, and the tendency for alternative copolymerizations increased with an increase in the electron-accepting nature of the comonomers in the order: styrene < methyl methacrylate < acrylonitrile. The selectivities between RVS and alkyl vinyl ether toward various polymer radicals were determined, and they were found to correlate with the e values of the monomers cor-responding to the attacking polymer radicals.

INTRODUCTION

In previous papers [1, 2] we reported the effects of the sulfur atom and the para-substituents in phenyl vinyl sulfides on their radical homopolymerizations and copolymerizations. It was found that these vinyl sulfide monomers could easily be homopolymerized by a radical initiator and that the Alfrey-Price Q values of these monomers were obtained as 0.45-0.47 from the copolymerizations with methyl methacrylate. These results strongly suggested that the 3d-orbital resonance between the growing radical and the adjacent sulfur atom in the transition state of the polymerization of vinyl sulfide monomers was significant. And the copolymerization reactivities of these monomers toward polystyryl and poly(methyl methacrylate) radicals were found to correlate with the Hammett σ constants of the para substituents. Recently, the importance of 3d-orbital resonance in the copolymerization of bis(phenylthio)ethylene derivatives [3] and ketene diethylmercaptal [4] was emphasized.

To confirm these points further, the radical copolymerizations of eight alkyl vinyl sulfides with styrene, methyl methacrylate, and acrylonitrile have been investigated in the present study. The alkyl groups in alkyl vinyl sulfides used have the following substituents: CH_3, C_2H_5, i-C_3H_7, n-C_4H_9, i-C_4H_9, t-C_4H_9, $C_6H_5CH_2$, and C_6H_5.

Regarding the copolymerization behavior of alkyl vinyl sulfides, Price and Zomlefer [5] reported the radical copolymerizations of methyl vinyl sulfide with styrene and methyl acrylate. Shostakovskii et al. [6] also studied radical and ionic copolymerizations of several alkyl vinyl sulfides.

EXPERIMENTAL

Preparation of Alkyl Vinyl Sulfides (RVS)

Methyl vinyl sulfide (MVS), ethyl vinyl sulfide (EVS), isopropyl vinyl sulfide (IPVS), n-butyl vinyl sulfide (BVS), isobutyl vinyl sulfide (IBVS), and t-butyl vinyl sulfide (t-BVS) were synthesized by the dehydration [7] of 2-hydroxyethyl alkyl sulfides [8], prepared from the reactions of the corresponding alkyl halides with 2-mercaptoethyl alcohol. Benzyl vinyl sulfide (BzVS) was prepared by dehydrochlorination of 2-chloroethylbenzyl sulfide with sodium t-butoxide. Phenyl vinyl sulfide (PVS) was obtained by the method described in the previous paper [1]. These RVS monomers were distilled in a stream of nitrogen just before use.

The physical and analytical data of these RVS monomers are summarized in Table 1.

Table 1. Physical and Analytical Data of Alkyl Vinyl Sulfides

RVS	Boiling point, °C/mm Hg	n_D^{20} [a]	Ref.	Observed		Calculated	
				C,%	H,%	C,%	H,%
MVS	67.0-67.2/760	1.4845 (1.4845)	[7]	48.86	8.30	48.59	8.16
EVS	90.0-91.0/760	1.4767 (1.4756)	[9]	54.64	9.28	54.49	9.15
IPVS	105.5/760	1.4645[b] (1.4645)[b]	[10]	58.76	9.86	58.74	9.79
BVS	51.6/23	1.4739[b] (1.4738)[b]	[11]	61.96	10.22	62.01	10.41
IBVS	69.5-71.0/93	1.4670[b] (1.4660)[b]	[10]	61.27	10.36	62.01	10.41
t-BVS	115/760	1.4626 (1.4615)	[12]	62.05	10.47	62.01	10.41
BzVS	80.1-81.3/4	1.5785 (1.5794)	[9]	72.27	6.83	71.95	6.71
PVS	60/4	1.5866[b] (1.5878)[b]	[13]	70.65	6.04	70.54	5.92

[a]Values in parentheses indicate the reported values.
[b]n_D^{25}

Table 2. The Results of Bulk Copolymerizations of RVS (M_2) with St (M_1) Initiated by AIBN at 60°C: [AIBN] = 5 × 10^{-3} mole/liter

RVS (M_2)	[M_2] in comonomer, mole %	Time, hr	Conversion, %	Copolymer C, %[a]	Copolymer [M_2], mole %[a]
MVS	13.4	2.5	5.8	91.24	3.1
	30.6	2.5	4.9	89.79	7.6
	44.0	4.2	17.2	88.73	10.8
	58.3	8.0	9.0	85.87	18.6
	67.7	11.0	10.3	83.45	26.1
	76.5	16.5	12.0	79.76	36.0
EVS	11.2	3.4	7.3	90.73 (0.79)	4.5 (2.5)
	22.2	4.2	6.9	89.72 (1.55)	7.7 (5.0)
	32.8	6.0	8.5	89.25 (2.56)	9.2 (8.2)
	43.2	6.3	8.6	87.75 (3.81)	13.6 (12.1)
	57.7	7.1	8.2	86.74 (5.20)	16.7 (16.5)
	63.1	8.1	7.3	83.32 (7.50)	26.5 (23.5)
	72.6	11.4	8.6	81.63 (12.20)	32.1 (37.4)
	82.0	16.6	10.3	76.96 (14.84)	44.4 (44.9)
	91.1	21.8	10.3	69.23 (22.25)	64.7 (65.1)
IPVS	13.4	2.5	7.1	91.10	3.4
	29.0	2.5	4.1	89.70	7.6
	42.8	4.2	17.7	87.05	15.7
	58.9	8.0	7.0	84.33	23.9
	73.1	11.0	7.6	80.64	35.1
	89.6	16.5	8.7	70.73	64.6
BVS	12.3	1.3	3.1	90.02	6.3
	22.4	3.0	5.4	87.60	7.8
	27.0	3.0	5.5	87.83	13.2
	34.1	4.2	6.9	88.88	10.0
	42.4	4.8	9.2	86.87	16.2
	46.3	6.0	8.0	87.13	15.4
	56.4	6.3	7.1	83.97	25.0
	59.0	7.8	8.4	86.55	17.1
	72.2	9.0	6.9	80.70	35.4
	72.7	7.5	6.5	80.66	35.7
	88.5	8.8	6.4	73.15	60.6

RVS (M_2)	[M_2] in comonomer, mole %	Time, hr	Conversion, %	Copolymer	
				C, %[a]	[M_2], mole %[a]
IBVS	9.7	1.5	2.7	90.64 (1.19)	7.1 (3.9)
	19.6	2.0	3.0	89.92 (1.68)	9.2 (5.4)
	30.2	2.4	2.8	89.60 (2.66)	10.2 (8.7)
	40.6	3.0	6.6	87.68 (3.83)	15.8 (12.2)
	51.7	4.8	3.3	86.60 (5.48)	19.0 (18.2)
	63.1	6.2	4.0	84.38 (7.63)	25.8 (25.5)
	75.0	7.0	4.5	81.40 (10.91)	34.9 (37.0)
t-BVS	13.6	2.0	5.6	90.90	3.9
	26.1	4.2	6.2	89.88	7.0
	37.4	7.0	8.5	88.62	10.8
	55.4	9.5	7.3	85.07	24.0
	70.2	12.8	7.3	81.44	33.2
	88.2	15.0	6.9	72.64	62.1
BzVS	8.6	2.1	4.5	91.00	4.2
	16.5	2.7	5.3	90.16	7.3
	25.3	3.0	5.5	90.42	6.3
	34.5	3.0	5.1	89.01	9.3
	44.1	3.4	4.7	86.84	20.1
	54.2	3.9	4.9	86.50	21.5
	64.8	15.9	5.0	85.03	27.7
	76.0	18.3	4.3	80.79	47.4
	87.6	32.0	4.2	78.01	62.1

[a]Values in parentheses indicate the sulfur content and the composition calculated from it.

Other Reagents

Styrene (St), methyl methacrylate (MMA), and acrylonitrile (AN) used as comonomers were purified by ordinary methods and distilled in a stream of nitrogen just before use. α,α'-Azobisisobutyronitrile (AIBN) used as a radical initiator was recrystallized twice from ethanol. Other reagents were used after purification.

Copolymerization

Copolymerizations of RVS with St, MMA, and AN were carried out in a sealed tube at 60°C. The required amounts of RVS, comonomer, and AIBN were charged into a hard glass tube, which was then degassed under vacuum by conventional freezing and thawing technique and sealed off under vacuum.

Most copolymerizations were carried out with shaking, in the absence of external light, to below 10% conversion. After copolymerization for a given time, the tube was opened and its contents were poured into a large amount of methanol to precipitate the copolymer.

The resulting copolymers with St and MMA were then purified by reprecipitating the benzene solution with excess methanol. In the case of the copolymers with AN, dimethylformamide was used as solvent and methanol as precipitant. Conversions were calculated from the weight of the dried copolymer obtained.

The composition of the copolymers was calculated from their elementary analyses of sulfur, carbon, or nitrogen, and the monomer reactivity ratios (r_1 and r_2) were obtained by the Fineman-Ross method and reconfirmed by the curve-fitting method.

RESULTS

Copolymerization of RVS with St

The results of the radical copolymerizations of RVS (M_2) with St (M_1) at 60°C are shown in Table 2.

Although the compositions of the copolymers in Table 2 were calculated from their carbon content, they were found to coincide with those calculated from the sulfur content in the cases of EVS and IBVS copolymerizations (see also Table 3).

Figure 1 shows, for example, the monomer-copolymer composition curve in the copolymerization of IBVS with St. When the results of the other RVS indicated in Table 2 were plotted in this figure, it was found that the monomer-copolymer composition curves varied only slightly with the kind of alkyl groups in RVS used.

From Table 2, the monomer reactivity ratios in these copolymerizations, and the Q_2 and e_2 values for RVS, were determined. The results are summarized in Table 3; the observed copolymerization parameters were in

Table 3. Copolymerization Parameters for RVS (M_2) - St (M_1) Systems at 60°C

RVS	r_1	r_2	Q_2	e_2
MVS	$5.0 (5.1)^a$	$0.15 (0.12)^a$	$0.31 (0.34)^a$	$-1.3 (-1.5)^a$
EVS	$4.4, 5.3^c (6.0 \pm 1.5)^b$	$0.12, 0.16^c (0.25 \pm 0.1)^b$	$0.45 (0.3)^b$	$-1.6 (-1.3)^b$
IPVS	4.3	0.20	0.31	-1.2
BVS	4.0	0.20	0.33	-1.2
IBVS	$4.0, 4.5^c$	$0.10, 0.15^c$	0.53	-1.7
t-BVS	4.7	0.20	0.26	-1.1
BzVS	4.7	0.27	–	–
PVS	$(3.88)^d$	$(0.36)^d$	–	–

[a] Data of Price et al. [5].
[b] Data of Shostakovskii et al. [6a].
[c] These values were calculated from the sulfur content in the copolymers.
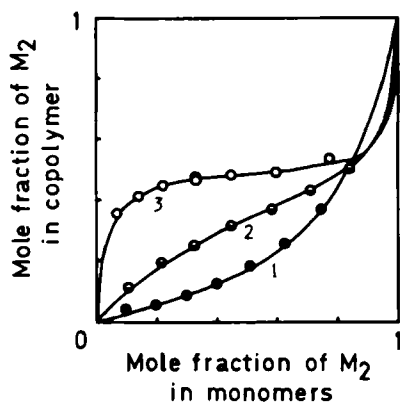[d] Data of Tsuda et al. [2].

Fig. 1. Monomer-copolymer composition curves for the radical copolymer-
izations of IBVS-St (1), IBVS-MMA (2), and IBVS-AN (3) systems at 60°C.

agreement with the reported values [5]. It was observed that the copoly-
merization parameters were almost unchanged with the nature of alkyl
groups in RVS.

Copolymerization of RVS with MMA

The results of the copolymerizations of three RVS (M_2) with MMA (M_1)
are shown in Table 4, from which the monomer-copolymer composition
curve for the IBVS-MMA copolymerization is indicated in Fig. 1, as an
example.

The monomer reactivity ratios obtained are shown in Table 5. Those
obtained for the EVS-MMA system were different from those reported by
Shostakovskii et al. [6], but our data seemed to be correct when compared
with the data of the other RVS systems. The relative reactivities ($1/r_1$) of
these RVS toward the poly(methyl methacrylate) radical were almost un-
changed with the structure of alkyl groups in RVS.

Copolymerization of RVS with AN

The results of the copolymerizations of three RVS (M_2) with AN (M_1)
are shown in Table 6, from which the monomer-copolymer composition
curve for the IBVS-AN copolymerization, for example, is also shown in
Fig. 1.

Table 4. The Results of Bulk Copolymerizations of RVS (M_2)
with MMA (M_1) Initiated by AIBN at 60°C:
[AIBN] = 5 × 10^{-3} mole/liter

RVS (M_2)	$[M_2]$ in comonomer, mole %	Time, hr	Conversion, %	Copolymer	
				S, %	$[M_2]$, mole %
EVS	14.7	0.42	4.0	6.32	19.3
	31.0	0.67	6.7	8.89	26.9
	45.5	0.92	9.9	10.80	32.6
	61.4	1.05	9.0	13.12	39.1
	74.9	2.00	13.8	15.53	45.8
	90.5	3.25	12.6	20.04	58.2
IPVS	27.6	2.00	14.1	8.11	25.5
	43.1	2.25	13.6	10.56	33.2
	59.2	3.13	16.4	12.87	40.5
	73.8	5.08	17.7	15.04	47.4
	88.9	7.42	13.7	18.84	59.5
IBVS	10.2	1.00	7.3	3.61	11.5
	21.0	1.30	14.9	6.17	19.9
	32.4	2.00	15.1	7.88	25.6
	44.4	2.00	13.3	9.81	32.2
	58.1	2.00	11.3	11.08	36.6
	70.5	2.00	9.4	13.03	43.5
	84.8	2.42	7.1	14.89	50.2

Table 5. The Monomer Reactivity Ratios in RVS (M_2)-MMA
(M_1) Copolymerizations at 60°C

RVS	r_1	r_2	$1/r_1$
EVS	0.93 (2.7 ± 1.5)[a]	0.07 (0.3 ± 0.1)[a]	1.08
IPVS	0.85	0.07	1.18
IBVS	0.94	0.04	1.06
PVS	0.85[b]	0.08[b]	1.18

[a]Data of Shostakovskii et al. [6a].
[b]Data of Tsuda et al. [2].

Table 6. The Results of Copolymerizations of RVS (M_2)
with AN (M_1) Initiated by AIBN at 60°C:
[AIBN] = 5 × 10^{-3} mole/liter

RVS (M_2)	[M_2] in comonomer, mole %	Time, min	Conversion, %	Copolymer	
				N, %	[M_2], mole %
BVS	11.1	10	4.6	11.39	37.6
	28.1	10	9.3	9.49	44.6
	42.7	10	11.0	8.85	47.6
	53.7	10	5.3	8.22	50.3
	66.5	10	8.4	8.11	50.8
	81.7	10	4.9	7.53	53.5
IBVS[a]	6.6	40	5.0	12.12	35.0
	14.1	40	6.7	10.75	41.5
	22.8	40	7.8	9.44	44.8
	32.9	40	8.0	8.84	47.9
	32.9[b]	120	8.6	9.13	46.4
	45.0	40	7.1	8.59	48.6
	59.6	40	5.0	8.55	48.8
	77.5	40	2.9	7.44	53.8
t-BVS	13.2	50	5.7	10.84	39.4
	27.2	50	36.0	9.74	43.8
	41.7	50	38.5	9.24	45.8
	52.7	50	30.8	8.77	47.9
	65.8	50	25.1	8.38	49.5
	81.0	50	16.3	8.27	50.1

[a][AIBN] = 1.09 × 10^{-3} mole/liter.
[b]In the absence of AIBN.

From Table 6, it was found that these copolymerizations proceeded at a
fast rate, even in the absence of AIBN initiator, and showed an increased
tendency for alternative copolymerizability. Similar conclusions were re-
ported in a previous paper [14] for the EVS-AN and PVS-AN copolymeri-
zations and for the copolymerizations of these sulfides with maleic anhydride.
Table 7 summarizes the monomer reactivity ratios obtained. Both the r_1

and r_2 values were quite small, also indicating that these systems show a good alternative copolymerizability.

Table 7. The Monomer Reactivity Ratios
in RVS (M_2)-AN (M_1) Copolymerizations
at 60°C

RVS	r_1	r_2	$r_1 r_2$
EVS	0.065[a]	0.055[a]	0.0036
BVS	0.097	0.046	0.0045
IBVS	0.068	0.050	0.0034
t-BVS	0.13	0.01	0.0013
PVS	0.11[a]	0.07[a]	0.0077

[a]Data from Ref. [14].

DISCUSSION

As can be seen from Table 3, the Q values for RVS were 0.3-0.5; they are quite a bit larger than those of the respective vinyl ethers (Q = 0.015 for ethyl vinyl ether [15]), but their e values (-1.1 ~ -1.7) were of almost the same order as those of vinyl ethers, indicating that these vinyl sulfides were classified into an electron-donating and reactive conjugate monomer. The observed large Q values for RVS emphasized that the electron-sharing 3d orbital resonance between the growing radical and the adjacent sulfur atom was significant in the transition state of the copolymerizations, as was first assumed by Price and Zomlefer [5]:

$$\sim\!\sim\!\sim CH_2 - \dot{C}H - \ddot{S} - R \quad \longleftrightarrow \quad \sim\!\sim\!\sim CH_2 - CH = \dot{S} - R \qquad (1)$$
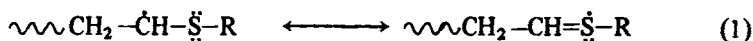
Regarding the polar and resonance effects of the alkylthio group in RVS, their IR [16], UV [5, 17], and NMR spectra [18] would provide some important information. The UV spectra of RVS, which provides data on the structure of the excited state, were especially significant for considering the actual structure of the growing RVS radicals. From such a standpoint, Price and Zomlefer [5] suggested a strong conjugative property of the sulfur atom in MVS.

Recently, Whery [19] reported that the alkylthio group on acid dissociation constants of substituted phenols participates in both electron-releasing

and -attracting conjugations in the ground state, and that the extent of both conjugations increases in a roughly equivalent fashion upon excitation, unless electron-releasing $p\pi$ conjugation is sterically inhibited. Accordingly, it may be assumed that RVS are more reactive monomers toward the polymer radical than the respective vinyl ethers.

From Tables 3, 5, and 7, it was noted that the effect of change in alkyl group of RVS on the reactivities toward polymer radicals was not as significant as that reported for alkyl acrylates [20] and methacrylates [21], whose reactivities were correlated with the polar substituent constants of their alkyl groups. A similar result was obtained for the effect of para substituents in PVS on their copolymerization reactivities, i.e., the observed Hammett ρ values were very small (+0.1 or -0.1 [2]). Also the UV λ_{max} (228 mμ except for t-BVS, BzVS, and PVS) and the IR stretching vibration band (1585-1588 cm^{-1}) of the C=C bond in RVS were almost unchanged with the nature of their alkyl groups.

As shown in Fig. 1, the copolymerization behavior of IBVS was significantly changed with the comonomers used. Namely, the copolymerization rate and alternative copolymerizability were found to increase in the order: St < MMA < AN. This order was essentially the same as that for the electron-accepting ability of these monomers. In a previous paper [14] we found that EVS and PVS quite easily underwent alternative copolymerization with the electron-accepting maleic anhydride. In this case, the donor-accepter interaction might be important between both the monomers, or between the growing radical and the reacting monomer in the transition state of alternative addition. Detailed results and discussion will be described in the next paper.

Although RVS showed high alternative copolymerizability toward AN monomer (see Table 7), the formation of a charge-transfer complex was not observed spectroscopically, contrary to the case of maleic anhydride for which the equilibrium constant can be estimated [14]. However, IBVS could easily copolymerize with AN even in the absence of radical initiator, indicating that a contact-type charge-transfer complex may form and participate at least in the initiation of this copolymerization.

It is interesting to compare the reactivities of RVS toward various polymer radicals with those of the respective alkyl vinyl ethers. If the r_1 values ($r_1 = k_{11}/k_{12}$ or k_{11}/k_{13}) for the copolymerizations of RVS (M$_2$) and alkyl vinyl ethers, RVE (M$_3$), with a given M$_1$ monomer are known, the relative reactivities (k_{12}/k_{13}) of RVS to RVE can be calculated easily. The results are summarized in Table 8, in which those determined by terpolymerization technique [25], which will be reported in the next paper, are also indicated.

Table 8. k_{12}/k_{13} Values at 60°C

M_1	M_2	M_3	r_1 k_{11}/k_{12}	k_{11}/k_{13}	k_{12}/k_{13}	Ref.
St	EVS	–	4.4	–		This work
St	–	EVE	–	90 ± 20	20.5	[15]
MMA	EVS	–	0.93	–		This work
MMA	–	OVE	–	10.1 ± 0.5[b]	10.9	[22]
MA	MVS	–	0.35	–		[5]
MA	–	EVE	–	3.3	9.4	[23]
AN	IBVS	–	0.068	–		This work
AN	–	IBVE	–	1.0	14.7	[24]
AN	IBVS	IBVE	–	–	7.35[c]	[25]
MAn	IBVS	IBVE	–	–	5.37[c]	[25]

[a]MA: methyl acrylate; MAn: maleic anhydride; EVE: ethyl vinyl ether; OVE: octyl vinyl ether; IBVE: isobutyl vinyl ether.
 [b]Values at 50°C.
 [c]Determined from terpolymerization technique [25].

If the effects of alkyl groups in both RVS and RVE, and the effects of the reaction temperature on their reactivities, are assumed to be neglected as mentioned above, the k_{12}/k_{13} values are considered to be a measure of the selectivity between RVS and RVE toward attack by a given polymer radical. Then the plots of k_{12}/k_{13} values in Table 8 with the e values of the M_1 monomers, which are used as a measure of the polarity of the respective polymer radicals, are shown in Fig. 2.

From Fig. 2, it was found that a straight-line relationship between log (k_{12}/k_{13}) and e_1 values was obtained except for the plot obtained from the reported r_1 values for AN-IBVS and AN-IBVE. The following empirical
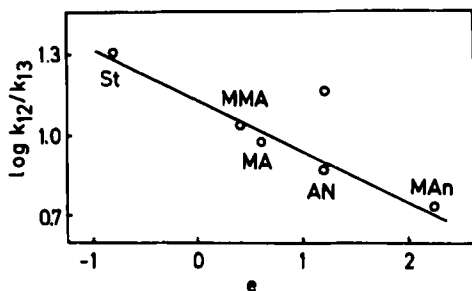
Fig. 2. Relationship between log (k_{12}/k_{13}) and e values of the monomers corresponding to the attacking polymer radicals.

equation was drawn:

$$\log (k_{12}/k_{13}) = -0.188 \; e_1 + 1.14 \qquad (2)$$

where e_1 indicates the polar nature (see Eq. 3) of the monomers corresponding to the polymer radicals. Hence the selectivities between RVS and RVE toward polymer radicals were found to be controlled by the polar character of the attacking polymer radicals.

These results might be understandable from the concept of the Q, e scheme reported by Alfrey and Price. Namely, the rate constant, k_{ij}, for the reaction of the growing M_i radical with the M_j monomer was assumed to be as follows:

$$k_{ij} = P_i Q_j \exp \{-e_i e_j\} \qquad (3)$$

where P_i is a general reactivity of the M_i radical, Q_j is a resonance stabilization of the M_j monomer, and e_i and e_j are the measures of polarities of M_i radical and M_j monomers, respectively. Accordingly, if this equation is applied for the selectivities (k_{12}/k_{13}) between RVS and RVE, the following equation is obtained:

$$\log (k_{12}/k_{13}) = \log (Q_2/Q_3) - \frac{1}{2.3} (e_2 - e_3)e_1 \qquad (4)$$

It is clear that Eq. (4) is in good agreement with Eq. (2), which was obtained empirically, indicating that the slope and the intercept of the straight line in Fig. 2 correspond to $-(e_2 - e_3)/2.3$ and log (Q_2/Q_3), respectively,

from Eq. (4). Hence the following equations were obtained from Eq. (2):

$$e_2 - e_3 = 0.43 \tag{5}$$

$$Q_2/Q_3 = 13.8 \tag{6}$$

These differences in polar and resonance factors between RVS and RVE were found to agree with those calculated by using the reported Q and e values for RVS and RVE (i.e., $Q_2 = 0.3 \sim 0.5$, $e_2 = -1.1 \sim -1.7$ for RVS (see Table 3), $Q_3 = 0.015$, $e_3 = -1.6$ for EVE [15], $Q_3 = 0.016 \pm 0.010$, $e_3 = -2.0 \pm 1.0$ for dodecyl vinyl ether [22].

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