

NOTES

Free-Radical Reactivity Parameters of 2,6-Dimethoxystyrene

INTRODUCTION

The 2,6-dimethoxy derivative of styrene has recently been prepared by a convenient synthetic procedure.¹ This monomer can be readily polymerized by free-radical, cationic, and anionic initiators.² Due to the substitution, poly(2,6-dimethoxystyrene) has a susceptibility to cationic grafting much greater than that of unsubstituted polystyrene¹ and a glass transition temperature about 25°C higher than unsubstituted polystyrene.³

In this communication we would like to report recent information on its reactivity and to use these reactivity parameters to explain its abnormal copolymerization behavior.

ABNORMAL COPOLYMERIZATION BEHAVIOR

The experimental data for the bulk copolymerizations of 2,6-dimethoxystyrene with styrene and methyl methacrylate at 60°C have already been published.³ The composition of the copolymer was determined from the relative peak heights in the ultraviolet absorption spectra of the copolymers in methylene chloride. The standard copolymer composition equation was used in differential form for low conversions to determine the reactivity ratios. The computerized nonlinear least-squares method of Tidwell and Mortimer⁴ has recently been used to determine the reactivity ratios. The results are given in Table I.

TABLE I
Reactivity Ratios of 2,6-Dimethoxystyrene at 60°C

Comonomers 1:2	r_1	r_2
2,6-Dimethoxystyrene:styrene	0.55	0.98
2,6-Dimethoxystyrene:methyl methacrylate	0.80	0.15

One interesting aspect of this monomer is that the expected relationship $r_{12}r_{23}r_{31} = r_{21}r_{32}r_{13}$ does not hold with styrene and methyl methacrylate as the other two monomers.⁵ Since this relationship is a direct outcome of the Q - e expression, the disagreement suggests that some if not all of the reactivity ratios of 2,6-dimethoxystyrene are abnormal. The reactivity parameters obtained from the reactivity ratios were then compared with the parameters for other monomers to determine whether or not they were consistent.

 Q - e VALUES

The Q and e values of 2,6-dimethoxystyrene were calculated from the reactivity ratios with styrene to be 1.91 and -1.59 , respectively.

The Q values for vinyl monomers have been related to the first ultraviolet absorption maxima by Ito et al.⁶ The ultraviolet absorption spectrum of 2,6-dimethoxystyrene was obtained in cyclohexane using a Cary 14 recording spectrophotometer and showed

the maximum at 218 m μ . This relatively high value of λ_{\max} found is consistent with the Q value obtained from the reactivity ratios with styrene.

The Q and e values for vinyl monomers can also be compared on a simple plot of e against Q (Fig. 1). The values tend to collect into four linear regions through which lines are drawn to a common intersection at Q and $e = 0$. There is a general tendency for electron-donating substituents to decrease the e value, as would be expected, and to increase the Q value. The 2,6-substitution is apparently more effective in lowering the e value than the 2,5-substitution.

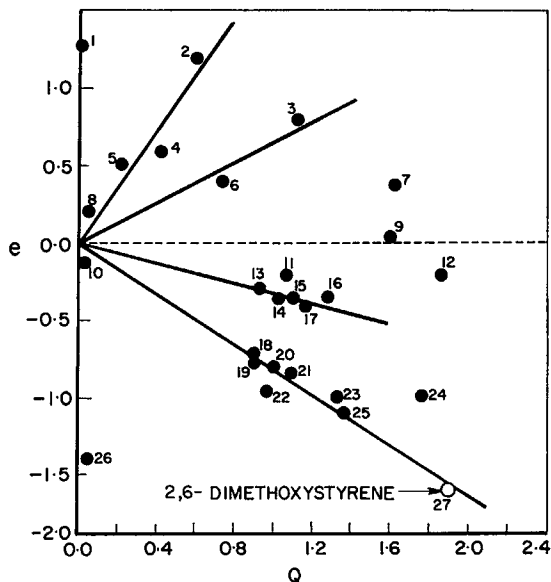


Fig. 1. Relationship between Q and e : (1) *trans*-dichloroethylene; (2) acrylonitrile; (3) methacrylonitrile; (4) methyl acrylate (5) pentachlorostyrene; (6) methyl methacrylate; (7) *p*-nitrostyrene; (8) vinyl chloride; (9) 2,5-dichlorostyrene; (10) vinyl acetate; (11) *m*-bromostyrene; (12) *p*-cyanostyrene; (13) *p*-trifluoromethylstyrene; (14) *m*-chlorostyrene; (15) *p*-bromostyrene; (16) *o*-chlorostyrene; (17) *p*-iodostyrene; (18) *m*-methylstyrene; (19) *o*-methylstyrene; (20) styrene; (21) *p*-methylstyrene; (22) 2,5-dimethylstyrene; (23) *p*-acetylaminostyrene; (24) 2,5-dimethoxystyrene (ref. 10); (25) *p*-methoxystyrene; (26) methyl vinyl sulfide; most data taken from ref. 11; (27) 2,6-dimethoxystyrene (present work).

A revised Q - e map was made by Kawabata et al.⁷ based on the e value of the styrene reference being redefined as zero. On this basis, for 2,6-dimethoxystyrene Q and e are 1.02 and -0.79 . On the revised Q - e map, 2,6-dimethoxystyrene belongs to the general group of conjugated monomers at the extreme of the lowest e value. Thus both the Q and e values of 2,6-dimethoxystyrene based on copolymerization with styrene are consistent with the Q and e values of other monomers, indicating that the reactivity ratios with styrene are normal.

Prediction of Reactivity Ratios of 2,6-Dimethoxystyrene with Methyl Methacrylate

The reactivity ratios with methyl methacrylate were predicted by two methods, the "patterns of free radical reactivity" approach of Bamford and Jenkins⁸ and the Q - e approach of Alfrey and Price.⁹

In the "patterns" approach, the reactivity ratios are given by the following equations:

$$\log r_1 = \sigma_1(\alpha_1 - \alpha_2) + (\beta_1 - \beta_2)$$

$$\log r_2 = \sigma_2(\alpha_2 - \alpha_1) + (\beta_2 - \beta_1).$$

The Hammett σ parameter characterizes the polarity of the substituent on the radical, for which greater electron-donating ability is demonstrated by a decreasing value of σ .

The β value is a measure of the polarity of the transition state for the monomer; α denotes the magnitude of the contribution of polar structure in the monomer to the transition state. Although σ and α can be determined independently, reasonably good agreement for common monomers was obtained with the relation

$$\alpha = -5.3\sigma.$$

For 2,6-dimethoxystyrene, the parameters were determined in two ways: using the styrene reactivity ratios and the α - σ relationship, and using both styrene reactivity ratios and the r_2 value for methyl methacrylate. The values of the reactivity parameters calculated are given in Table II.

TABLE II
Parameters from the "Patterns" Treatment

Using the modified equation	Using the r_2 value with methyl methacrylate
$\alpha = 1.22$	1.19
$\beta = 4.87$	4.87
$\sigma = -0.23$	-0.24

The electron-donating characteristics of the monomer are reflected in the high value of α and the low value of σ .

Using the previously determined parameters, the reactivity ratios have been calculated for copolymerizing 2,6-dimethoxystyrene with methyl methacrylate. These calculated values can be compared with the experimentally determined values in Table III.

Both the Q - e approach and the "patterns" treatment predict the value of r_2 reasonably well. Neither scheme, however, predicts the value of r_1 very closely. This disagreement suggests that the value for r_1 is anomalous, since the previous comparisons of the Q and e

TABLE III
Prediction of Reactivity Ratios

Basis	r_1	r_2
	Predicted	
1. Q - e values for 2,6-dimethoxystyrene determined with styrene; Q - e values for methyl methacrylate taken from the literature	0.113	0.18
2. Modified "patterns" treatment using α and β values determined with styrene; the α - σ relationship; and the α , β , and σ values for methyl methacrylate taken from the literature	0.22	0.25
3. Full "patterns" treatment using the r_2 value with methyl methacrylate to determine the σ value separately	0.21	—
	Found	
	0.80	0.15

values for 2,6-dimethoxystyrene with the general behavior of the Q and e values for other monomers indicate that copolymerization with styrene proceeds normally. This anomalous reactivity ratio refers to the relative ease with which the 2,6-dimethoxystyryl radical adds to its own monomer and to methyl methacrylate. The anomalously high value of this reactivity ratio suggests that the addition of methyl methacrylate is being hindered somewhat sterically due to its 1,1-disubstitution and the bulky 2,6-dimethoxyphenyl group on the radical.

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