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The reactivity of initiator radicals
V. The application of the revised patterns scheme

A.D. Jenkins*

School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton BN1 9QJ, UK

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Abstract

Recently, the interpretation of the reactivity of polymer radicals has been developed by means of some improvements to the so-called Patterns Scheme, itself an advance over the Alfrey-Price *Q-e* Scheme. Using the reactivity of a radical with styrene as a measure of its "general" (i.e. thermodynamic) reactivity, it has been shown that a parameter denoting radical polarity can easily be deduced from polymerisation data, and that these 2 parameters can be used quantitatively to characterise the behaviour of that radical in copolymerisations in general. It thus becomes possible to forecast monomer reactivity ratios with much greater precision than heretofore. The present article extends this treatment to the reactions of initiator radicals with monomers. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Radical polymerisation; Monomer reactivity ratios; Radical initiation

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1. Introduction

The Revised Patterns Scheme [1–4] has been used to account for the copolymerisation reactivity of over 100 monomers. In effect, the scheme predicts the relative reactivity of a chosen polymer radical when confronted with a choice of 2 alternative monomers to which it may add; in the binary copolymerisation of 2 monomers, it predicts the values of the 2 monomer reactivity ratios. The question may validly be asked whether the scheme can be adapted to provide a useful analysis of the similar situation experienced by a radical produced by the homolytic breakdown of an initiator, i.e. an initiator radical. A brief development of the basic concepts of the Revised Patterns Scheme leads to a simple equation that provides the relative rates of reaction of an initiator radical with 2 monomers, and the results compare favourably with much experimental data in the literature.

2. The general equation for the reactions of an initiator radical

We begin by considering the basic equations of the Revised Patterns Scheme [2,3].

$$\log r_{12} = \log r_{1S} - u_2 \cdot \pi_1 - v_2, \tag{1}$$

$$\log r_{21} = \log r_{2S} - u_1 \cdot \pi_2 - v_1. \tag{2}$$

Here, species 1 and 2 are comonomers; r_{12} is the monomer reactivity ratio for a radical terminated by a unit derived from monomer 1 in copolymerisation with species 2, and r_{1S} is the monomer reactivity ratio for a radical terminated by a unit derived from monomer 1 in copolymerisation with styrene (denoted by subscript S). $\log r_{1S}$ and π_1 quantitatively characterise the general reactivity and the polarity, respectively, of the radical of type 1 (i.e. a polymer radical in which the terminal unit is derived from monomer 1), while v_2 and u_2 quantitatively characterise the general reactivity and the polarity, respectively, of monomer 2, and *mutatis mutandis*.

If we now consider, as a separate reaction, the copolymerisation of monomers 1 and 3, the corresponding equations are

$$\log r_{13} = \log r_{1S} - u_3 \cdot \pi_1 - v_3, \tag{3}$$

$$\log r_{31} = \log r_{3S} - u_1 \cdot \pi_3 - v_1. \tag{4}$$

The ratio of rates of the reactions of species 1 with 2 and 3 is then derived by subtraction of Eq. (3) from Eq. (1), thus

$$\log r_{12} - \log r_{13} = -u_2 \cdot \pi_1 - v_2 + u_3 \cdot \pi_1 + v_3, \tag{5}$$

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* Tel.: + 44-0-1273-845410; fax: + 44-0-1273-845410.
E-mail address: adjjj@jjadj.u-net.com (A.D. Jenkins)

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Table 1
Data for the calculation of π_1 according to Eq. (11). The monomers are indicated by abbreviations, the key to which is as follows. AC, acrolein; AN, acrylonitrile; MA, methyl acrylate; MAN, methacrylonitrile; VA, vinyl acetate; MM, methyl methacrylate; S, styrene; VC, vinyl chloride; VC2, vinylidene chloride; VP-2, 2-vinyl pyridine; VP-4, 4-vinyl pyridine; VEE, vinyl ethyl ether; and alphaMeS, α-methyl styrene

Radical 1	Monomer 2	u_2	v_2	k_{12} ($\mathrm{M}^{-1}\ \mathrm{s}^{-1}$)	k_{12}/k_{13}	$\log(k_{12}/k_{13})$	$[\log(k_{12}/k_{13}) - v_2]$
Benzoyloxy	AN	−2.6	0.42		< 0.05		
	VA	−0.44	−1.56		0.360	−0.444	1.116
	MM	−1.18	0.23		0.120	−0.921	−1.151
	S	0	0		1.000	0.00	0.000
2-Cyano-2-propyl	AN	−2.6	0.42	2020	0.669	−0.175	−0.595
	MA	−2.34	0.16	367	0.226	−0.646	−0.806
	MAN	−2.08	0.44	1060	0.390	−0.409	−0.849
	VA	−0.44	−1.56	41	0.021	−1.678	−0.118
	MM	−1.18	0.23	1590	0.610	−0.215	−0.445
	S	0.0	0.0	2410	1.000	0.000	0.000
	VC2	−1.34	−0.24	603	0.250	−0.602	−0.362
	VEE	1.11	−2	108	0.044	−1.357	0.643
	VP-4	−0.94	0.3	1560	0.649	−0.188	−0.488
	VP-2	−0.98	0.32	2040	1.090	0.037	−0.283
	AlphaMeS	−0.04	−0.03	2310	0.954	−0.020	0.010
	AC	−2.75	0.59	1200	0.497	−0.304	−0.894
Hydroxymethyl	AN	−2.6	0.42	1100 000	47.826	1.680	1.260
	MA	−2.34	0.16	710 000	30.870	1.490	1.330
	MAN	−2.08	0.44	670 000	29.130	1.464	1.024
	VA	−0.44	−1.56	590	0.026	−1.591	−0.031
	MM	−1.18	0.23	600 000	26.087	1.416	1.186
	S	0.0	0	23 000	1.000	0.000	0.000
	VC2	−1.34	−0.24	53 000	2.304	0.363	0.603
	VC	−0.9	−1.16	5000	0.217	−0.663	0.497
	AlphaMeS	−0.04	−0.03	28 000	1.217	0.085	0.115
	AC	−2.75	0.59	2100 000	91.304	1.960	1.370
tert-Butyl	S	0.0	0	132 000	1.000	0.000	0.000
	VA	−0.44	−1.56	4200	0.032	−1.497	0.063
	VC	−0.9	−1.16	16 500	0.125	−0.903	0.257
	VEE	1.11	−2	390	0.003	−2.530	−0.530
	VC2	−1.34	−0.24	350 000	2.652	0.423	0.663
Methyl	AN	−2.6	0.42	610 000	2.346	0.370	−0.050
	MA	−2.34	0.16	340 000	1.308	0.117	−0.043
	MAN	−2.08	0.44	490 000	1.885	0.275	−0.165
	VA	−0.44	−1.56	10 000	0.038	−1.415	0.145
	MM	−1.18	0.23	490 000	1.885	0.275	0.045
	S	0.0	0	260 000	1.000	0.000	0.000
	VC2	−1.34	−0.24	230 000	0.885	−0.053	0.187
	VC	−0.9	−1.16	20 000	0.077	−1.114	0.046
	AlphaMeS	−0.04	−0.03	300 000	1.154	0.062	0.092
	AC	−2.75	0.59	740 000	2.846	0.454	−0.136
	VEE	1.11	−2	14 000	0.054	−1.269	0.731
2-Hydroxy-2-propyl	AN	−2.6	0.42	130000 000	228.070	2.358	1.938
	MA	−2.34	0.16	37500 000	65.789	1.818	1.658
	MAN	−2.08	0.44	38000 000	66.667	1.824	1.384
	MM	−1.18	0.23	15500 000	27.193	1.434	1.204
	S	0.0	0	570 000	1.000	0.000	0.000
	AlphaMeS	−0.04	−0.03	200 000	0.351	−0.455	−0.425
	AC	−2.75	0.59	250000 000	438.596	2.642	2.052
Benzyl	AN	−2.6	0.42	2200	2.000	0.301	−0.119
	MA	−2.34	0.16	430	0.391	−0.408	−0.568
	MAN	−2.08	0.44	6600	6.000	0.778	0.338
	VA	−0.44	−1.56	15	0.014	−1.865	−0.305
	MM	−1.18	0.23	2100	1.909	0.281	0.051

Table 1 (*continued*)

Radical 1	Monomer 2	u_2	v_2	k_{12} (M^{-1} s^{-1})	k_{12}/k_{13}	$\log(k_{12}/k_{13})$	$[\log(k_{12}/k_{13}) - v_2]$
	S	0	0	1100	1.000	0.000	0.000
	VC2	−1.34	−0.24	460	0.418	−0.379	−0.139
	VEE	1.11	−2	14	0.013	−1.895	0.105
	VP-4	−0.94	0.3	6700	6.091	0.785	0.485
	AlphaMeS	−0.04	−0.03	850	0.773	−0.112	−0.082
	AC	−2.75	0.59	2500	2.273	0.357	−0.233
Malonyl (I)	AN	−2.6	0.42	149000	0.130	−0.888	−1.308
	MA	−2.34	0.16	112000	0.097	−1.011	−1.171
	MAN	−2.08	0.44	600000	0.522	−0.283	−0.723
	VA	−0.44	−1.56	395000	0.343	−0.464	1.096
	MM	−1.18	0.23	1060000	0.922	−0.035	−0.265
	S	0	0	1150000	1.000	0.000	0.000
	VC2	−1.34	−0.24	388000	0.337	−0.472	−0.232
	VEE	1.11	−2	302000	0.263	−0.581	−1.419
	AlphaMeS	−0.04	−0.03	1330000	1.157	0.063	0.093
	AC	−2.75	0.59	110000	0.096	−1.019	−1.609
Cumyl	AN	−2.6	0.42	2200	1.833	0.263	−0.157
	MA	−2.34	0.16	800	0.667	−0.176	−0.336
	MM	−1.18	0.23	2700	2.250	0.352	0.122
	S	0	0	1200	1.000	0.000	0.000
Cyanomethyl	AN	−2.6	0.42	110000	0.289	−0.538	−0.958
	MA	−2.34	0.16	110000	0.289	−0.538	−0.698
	MAN	−2.08	0.44	170000	0.447	−0.349	−0.789
	VA	−0.44	−1.56	13000	0.034	−1.466	0.094
	MM	−1.18	0.23	240000	0.632	−0.200	−0.430
	S	0	0	380000	1.000	0.000	0.000
	VC2	−1.34	−0.24	33000	0.087	−1.061	−0.821
	VEE	1.11	−2	43000	0.113	−0.946	1.054
	AlphaMeS	−0.04	−0.03	660000	1.737	0.240	0.270
	AC	−2.75	0.59	25000	0.066	−1.182	−1.772
tert-Butylcarbonylmethyl	AN	−2.6	0.42	540000	0.284	−0.546	−0.966
	MA	−2.34	0.16	490000	0.258	−0.589	−0.749
	MAN	−2.08	0.44	910000	0.479	−0.320	−0.760
	VA	−0.44	−1.56	65000	0.034	−1.466	0.094
	MM	−1.18	0.23	1300000	0.684	−0.165	−0.395
	S	0	0	1900000	1.000	0.000	0.000
	VC2	−1.34	−0.24	270000	0.142	−0.847	−0.607
	VEE	1.11	−2	150000	0.079	−1.103	0.897
	AlphaMeS	−0.04	−0.03	3900000	2.053	0.312	0.342
	AC	−2.75	0.59	380000	0.200	−0.699	−1.289
Malonyl (II)	AN	−2.6	0.42	137000	1.370	0.137	−0.283
	AC	−2.75	0.59	210000	2.100	0.322	−0.268
	MA	−2.34	0.16	119000	1.190	0.076	−0.084

i.e.

$$\log\frac{r_{12}}{r_{13}} = -\pi_1(u_2 - u_3) - (v_2 - v_3). \qquad (6)$$

Remembering that $r_{12} = k_{11}/k_{12}$ and $r_{13} = k_{11}/k_{13}$, we arrive at the result:

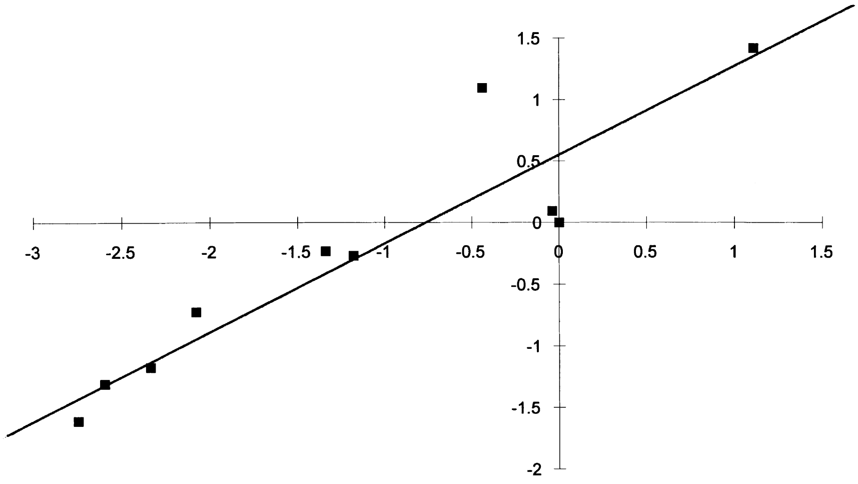
$$\log\frac{k_{12}}{k_{13}} = \pi_1(u_2 - u_3) + (v_2 - v_3). \qquad (7)$$

It is thus found that the ratio of the rates at which the initiator radical (1) reacts with the monomers (2 and 3) is given by a simple relationship involving the polarity parameter of the radical (π_1) and the *u* and *v* parameters of the 2 monomers.

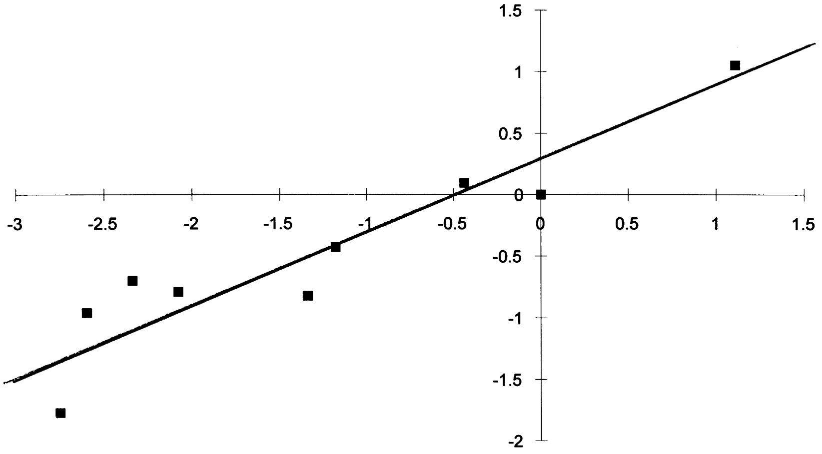
3. Determination of π_1, the polarity parameter for the radical

Now, if it is supposed that species 1 is not a polymer radical but a radical derived from the initiator, use of Eq. (7) necessitates the evaluation of the only parameter

(a) Malonyl I



(b) Cyanomethyl



(c) (*tert*-Butoxy)carbonylmethyl

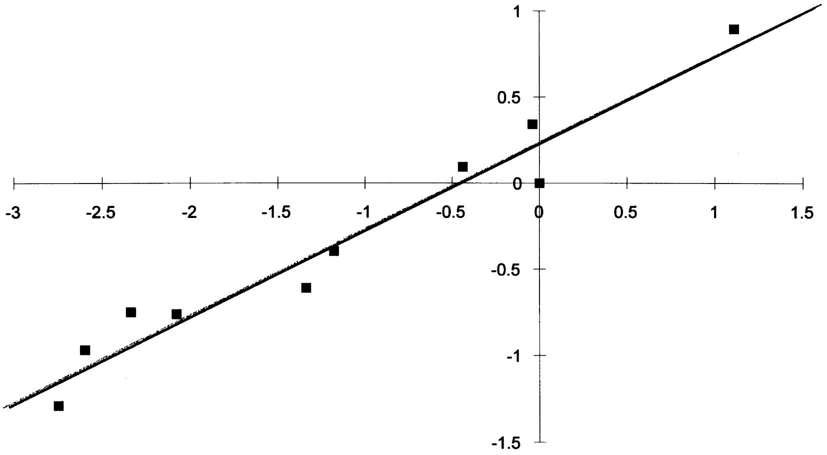
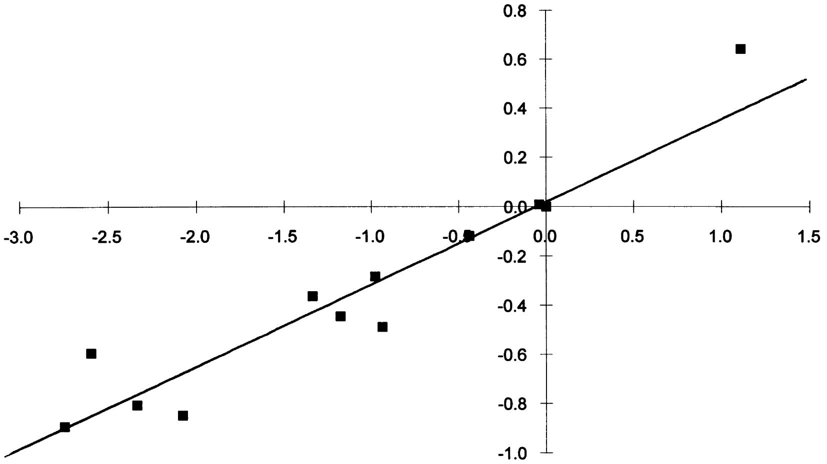
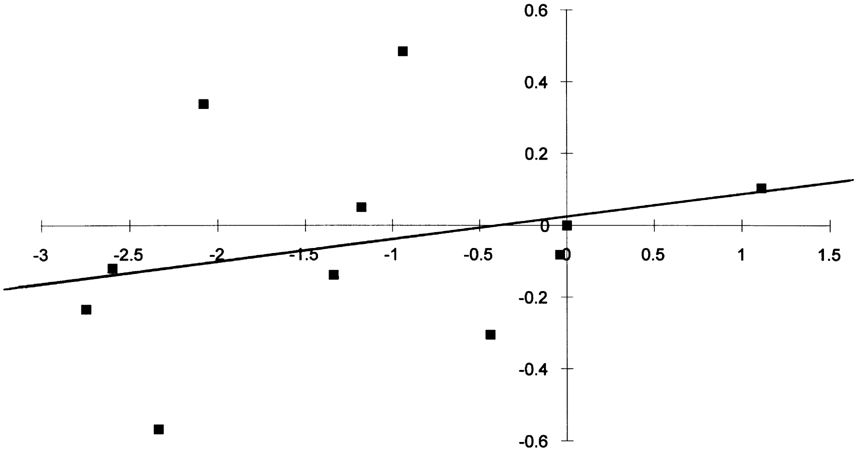


Fig. 1. Plots of the data for ten initiator radicals according to Eq. (11). In each case, the value of π_1 is determined from the slope of the line. Abscissa, u_2; ordinate, $[\log(k_{12}/k_{1S}) - v_2]$.

(d) 2-Cyano-2-propyl



(e) Benzyl



(f) Methyl

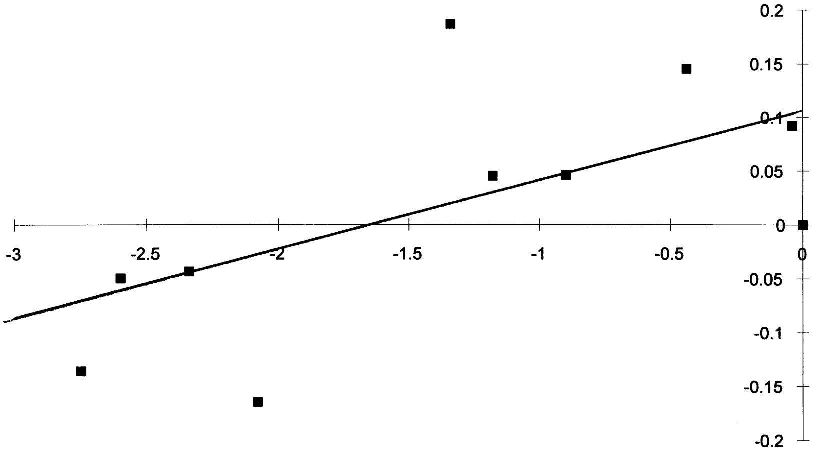
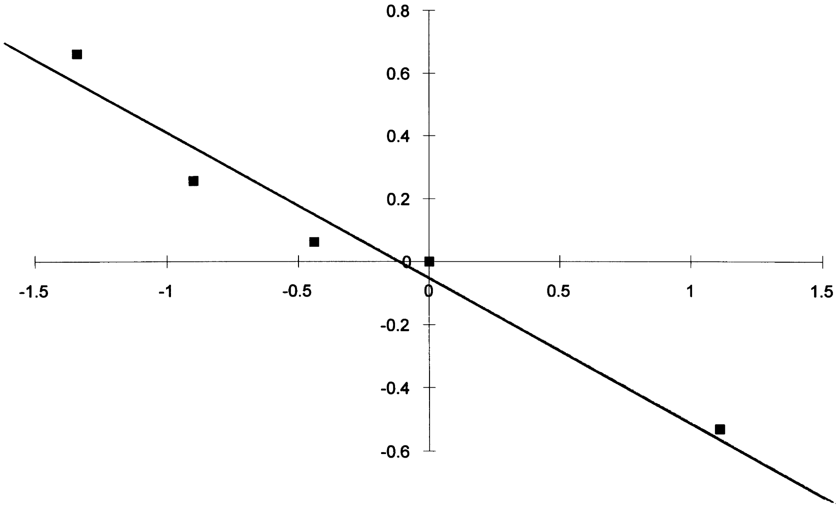
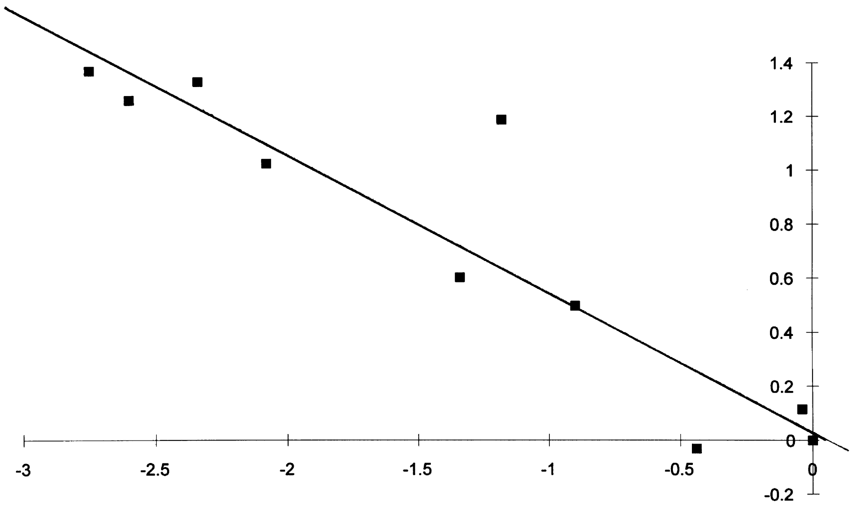


Fig. 1. (*continued*)

(g) *tert*-Butyl



(h) Hydroxymethyl



(i) 2-Hydroxy-2-propyl

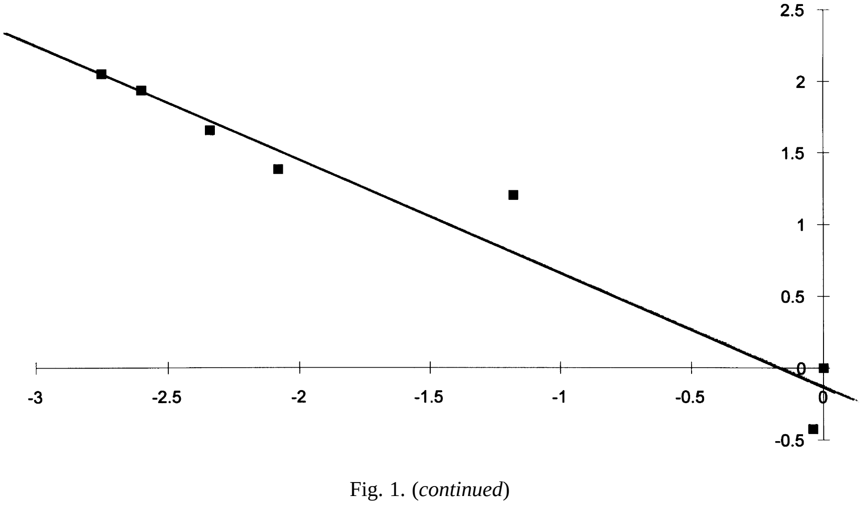


Fig. 1. (*continued*)

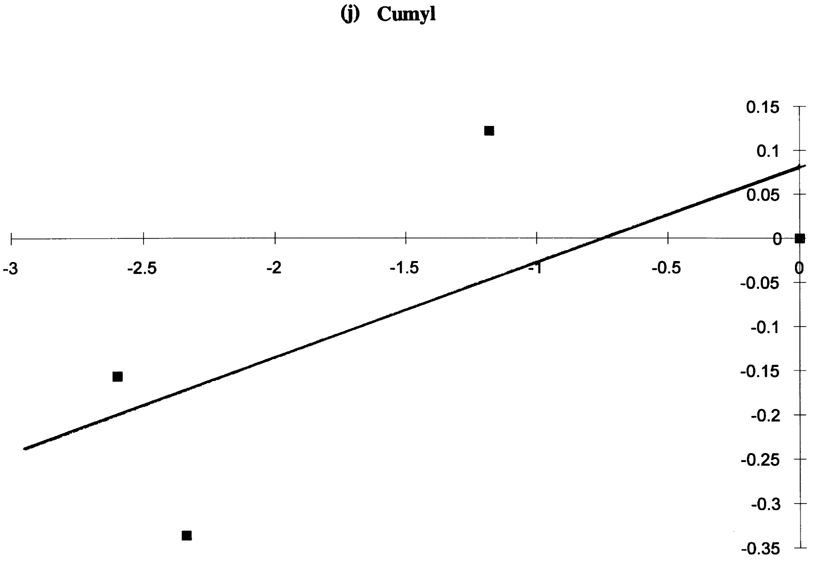

(j) Cumyl

Fig. 1. (*continued*)

pertaining to its reactivity, which is π_1. This is very easily determined by solution of Eq. (7) if we already know the relative reactivity of the radical towards 2 monomers with known u and v parameters; 143 monomers with known u and v parameters have been listed previously [4], so the minimum information that is required consists of the values of k_{12}/k_{13} for a couple of suitable monomers, preferably with very different polarities, e.g. styrene (S) and acrylonitrile (A). To proceed in this way is to follow the AS Scheme, described previously [2,3], and π_1 is then given by the rearrangement of Eqs. (7) and (8).

$$\pi_1 = \frac{\log\dfrac{k_{1\mathrm{A}}}{k_{1\mathrm{S}}} - (v_\mathrm{A} - v_\mathrm{S})}{u_\mathrm{A} - u_\mathrm{S}}. \tag{8}$$

A better procedure, if data can be found for more than the 2 reference monomers cited (styrene and acrylonitrile), is to rearrange Eq. (7) in the following way:

$$\log\frac{k_{12}}{k_{13}} - (v_2 - v_3) = \pi_1(u_2 - u_3), \tag{9}$$

and then to plot $[\log(k_{12}/k_{13}) - (v_2 - v_3)]$ as ordinate against $(u_2 - u_3)$ as abscissa for all the available monomer combinations in order to determine the slope, which is equal to π_1. The fact that such a plot turns out to be linear would in itself be a confirmation of the validity of the applicability of the revised patterns scheme to the reactions of initiator radicals. This procedure is an extension of the UV Scheme, described previously [2,3].

A particularly simple situation exists if styrene is chosen to be monomer 3 because we then [2–4] have $u_3 = v_3 = 0$, and Eqs. (7) and (9) become Eqs. (10) and (11), respectively.

$$\log\frac{k_{12}}{k_{1\mathrm{S}}} = \pi_1 \cdot u_2 + v_2, \tag{10}$$

$$\log\frac{k_{12}}{k_{1\mathrm{S}}} - v_2 = \pi_1 \cdot u_2. \tag{11}$$

To test Eq. (11), the data in Table 1 have been taken from the work of Bevington and of Fischer for the following

Table 2
π_1, $(\sigma_\mathrm{p})_1$ and other data for the radicals

Radical	π_1	Slope	Intercept	Range	Reduced intercept	$(\sigma_\mathrm{p})_1$
Malonyl I	+ 0.702	0.800	0.141	1.2	0.120	0.90
Cyanomethyl	+ 0.571	0.888	0.074	1.0	0.074	0.67
(*tert*-Butoxy)CM	+ 0.503	0.925	0.076	1.0	0.076	0.45
Malonyl II	+ 0.483					0.90
Cyano-isopropyl	+ 0.359	1.050	0.014	1.0	0.014	0.35
Cumyl	+ 0.113					− 0.33
Benzyl	+ 0.064	0.890	− 0.163	2.1	0.078	− 0.01
Methyl	+ 0.063	0.854	0.027	2.3	0.012	0
tert-Butyl	− 0.452	0.876	− 0.043	2.6	0.016	− 0.48
Hydroxymethyl	− 0.506	1.05	2.09	100	0.024	− 0.36
Hydroxy-isopropyl	− 0.750	1.02	− 5.53	440	0.013	− 0.68

Table 3
Data for the calculation of k_{12}/k_{13} from Eq. (7), and comparison with experimental results. Symbols for monomers as for Table 1

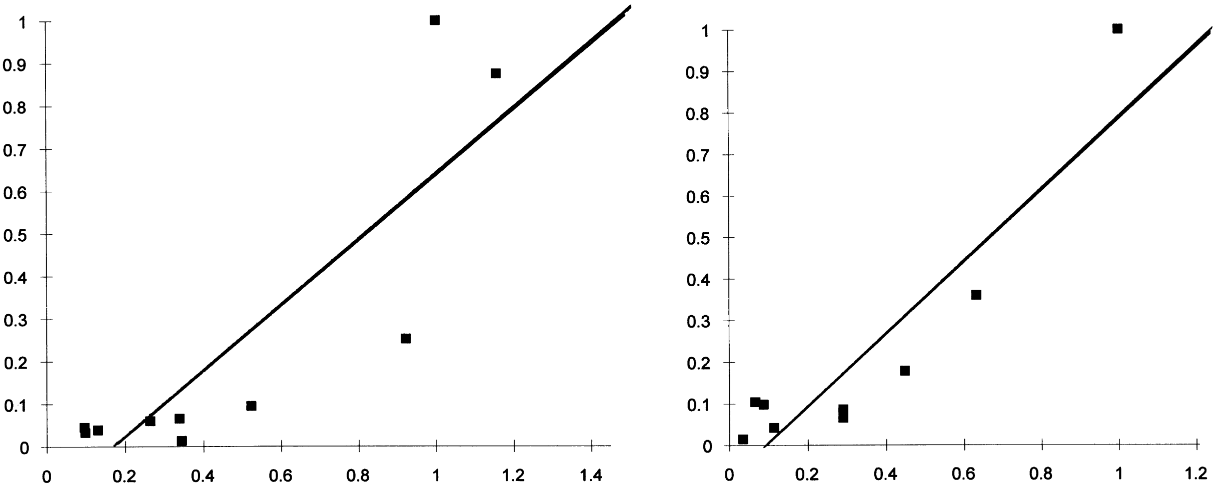
Radical 1	Monomer 2	u_2	v_2	$\pi_1 \cdot u_2$	$(\pi_1 \cdot u_2) + v_2$	$\ln[(\pi_1 \cdot u_2) + v_2]$	k_{12}/k_{13}(calc.)	k_{12} (exp. M^{-1} s^{-1})	k_{12}/k_{13} (exp.)
Benzoyloxy	AN	−2.6	0.42	−2.535	−2.115	−4.871	0.008		< 0.05
	VA	−0.44	−1.56	−0.429	−1.989	−4.581	0.010		0.360
$\pi = +0.975$	MM	−1.18	0.23	−1.151	−0.921	−2.120	0.120		0.120
	S	0	0	0.000	0.000	0.000	1.000		1.000
2-cyano-2-propyl	AN	−2.6	0.42	−0.902	−0.482	−1.111	0.329	2020	0.838
	MA	−2.34	0.16	−0.812	−0.652	−1.502	0.223	367	0.152
$\pi = +0.347$	MAN	−2.08	0.44	−0.722	−0.282	−0.649	0.523	1060	0.440
	VA	−0.44	−1.56	−0.153	−1.713	−3.944	0.019	41	0.017
	MM	−1.18	0.23	−0.409	−0.179	−0.413	0.661	1590	0.660
	S	0	0	0.000	0.000	0.000	1.000	2410	1.000
	VC2	−1.34	−0.24	−0.465	−0.705	−1.624	0.197	603	0.250
	VEE	1.11	−2	0.385	−1.615	−3.719	0.024	108	0.045
	VP-4	−0.94	0.3	−0.326	−0.026	−0.060	0.941	1560	0.647
	VP-2	−0.98	0.32	−0.340	−0.020	−0.046	0.955	2040	0.846
	AlphaMeS	−0.04	−0.03	−0.014	−0.044	−0.101	0.904	2310	0.959
	AC	−2.75	0.59	−0.954	−0.364	−0.839	0.432	1200	0.498
Hydroxymethyl	AN	−2.6	0.42	1.316	1.736	3.997	54.439	1100 000	47.826
	MA	−2.34	0.16	1.217	1.377	3.171	23.826	710 000	30.870
$\pi = -0.506$	MAN	−2.08	0.44	1.052	1.492	3.437	31.099	670 000	29.130
	VA	−0.44	−1.56	0.223	−1.337	−3.080	0.046	590	0.026
	MM	−1.18	0.23	0.597	0.827	1.905	6.718	600 000	26.087
	S	0	0	0.000	0.000	0.000	1.000	23 000	1.000
	VC2	−1.34	−0.24	0.678	0.438	1.009	2.742	53 000	2.304
	VC	−0.9	−1.16	0.455	−0.705	−1.623	0.197	5000	0.217
	AlphaMeS	−0.04	−0.03	0.020	−0.010	−0.022	0.978	28 000	1.217
	AC	−2.75	0.59	1.392	1.982	4.563	95.908	2100 000	91.304
tert-Butyl	S	0	0	0.000	0.000	0.000	1.000	132 000	1.000
	VA	-0.44	−1.56	0.200	−1.360	−3.133	0.044	4200	0.032
$\pi = -0.454$	VC	−0.9	−1.16	0.409	−0.751	−1.730	0.177	16 500	0.125
	VEE	1.11	−2	−0.504	−2.504	−5.767	0.003	390	0.003
	VC2	−1.34	−0.24	0.608	0.368	0.848	2.336	350 000	2.652
Methyl	AN	−2.6	0.42	−0.164	0.256	0.590	1.804	610 000	2.346
	MA	−2.34	0.16	−0.147	0.013	0.029	1.029	340 000	1.308
$\pi = 0.063$	MAN	−2.08	0.44	−0.131	0.309	0.712	2.037	490 000	1.885
	VA	−0.44	−1.56	−0.028	−1.588	−3.657	0.026	10 000	0.038
	MM	−1.18	0.23	−0.074	0.156	0.358	1.431	490 000	1.885
	S	0	0	0.000	0.000	0.000	1.000	260 000	1.000
	VC2	−1.34	−0.24	−0.084	−0.324	−0.747	0.474	230 000	0.885
	VC	−0.9	−1.16	−0.057	−1.217	−2.802	0.061	20 000	0.077
	AlphaMeS	−0.04	−0.03	−0.003	−0.033	−0.075	0.928	300 000	1.154
	AC	−2.75	0.59	−0.173	0.417	0.960	2.611	740 000	2.846
	VEE	1.11	−2	0.070	−1.930	−4.445	0.012	14 000	0.054
2-Hydroxy-2-propyl	AN	−2.6	0.42	1.950	2.370	5.458	234.654	130000 000	228.070
	MA	−2.34	0.16	1.755	1.915	4.410	82.290	37500 000	65.789
$\pi = -0.75$	MAN	−2.08	0.44	1.560	2.000	4.606	100.083	38000 000	66.667
	MM	−1.18	0.23	0.885	1.115	2.568	13.038	15500 000	27.193
	S	0	0	0.000	0.000	0.000	1.000	570 000	1.000
	AlphaMeS	−0.04	−0.03	0.030	0.000	0.000	1.000	200 000	0.351
	AC	−2.75	0.59	2.063	2.653	6.109	449.757	250000 000	438.596
Benzyl	AN	−2.6	0.42	−0.165	0.255	0.586	1.798	2200	2.000
	MA	−2.34	0.16	−0.149	0.011	0.026	1.026	430	0.391
$\pi = 0.0636$	MAN	−2.08	0.44	−0.132	0.308	0.709	2.031	6600	6.000
	VA	−0.44	−1.56	−0.028	−1.588	−3.657	0.026	15	0.014
	MM	−1.18	0.23	−0.075	0.155	0.357	1.429	2100	1.909
	S	0	0	0.000	0.000	0.000	1.000	1100	1.000
	VC2	−1.34	−0.24	−0.085	−0.325	−0.749	0.473	460	0.418

Table 3 (*continued*)

Radical 1	Monomer 2	u_2	v_2	$\pi_1 \cdot u_2$	$(\pi_1 \cdot u_2) + v_2$	$\ln[(\pi_1 \cdot u_2) + v_2]$	k_{12}/k_{13}(calc.)	k_{12} (exp. $M^{-1}\ s^{-1}$)	k_{12}/k_{13} (exp.)
	VEE	1.11	− 2	0.071	− 1.929	− 4.443	0.012	14	0.013
	VP-4	− 0.94	0.3	− 0.060	0.240	0.553	1.739	6700	6.091
	AlphaMeS	− 0.04	− 0.03	− 0.003	− 0.033	− 0.075	0.928	850	0.773
	AC	− 2.75	0.59	− 0.175	0.415	0.956	2.601	2500	2.273
Malonyl (l)	AN	− 2.6	0.42	− 1.825	− 1.405	− 3.236	0.039	149 000	0.130
	MA	− 2.34	0.16	− 1.643	− 1.483	− 3.415	0.033	112 000	0.097
$\pi = 0.702$	MAN	− 2.08	0.44	− 1.460	− 1.020	− 2.349	0.095	600 000	0.522
	VA	− 0.44	− 1.56	− 0.309	− 1.869	− 4.304	0.014	395 000	0.343
	MM	− 1.18	0.23	− 0.828	− 0.598	− 1.378	0.252	1060 000	0.922
	S	0	0	0.000	0.000	0.000	1.000	1150 000	1.000
	VC2	− 1.34	− 0.24	− 0.941	− 1.181	− 2.719	0.066	388 000	0.337
	VEE	1.11	− 2	0.779	− 1.221	− 2.811	0.060	302 000	0.263
	AlphaMeS	− 0.04	− 0.03	− 0.028	− 0.058	− 0.134	0.875	1330 000	1.157
	AC	− 2.75	0.59	− 1.931	− 1.341	− 3.087	0.046	110 000	0.096
Cumyl	AN	− 2.6	0.42	− 0.294	0.126	0.291	1.337	2200	1.833
	MA	− 2.34	0.16	− 0.264	− 0.104	− 0.240	0.786	800	0.667
$\pi = + 0.113$	MM	− 1.18	0.23	− 0.133	0.097	0.233	1.249	2700	2.250
	S	0	0	0.000	0.000	0.000	1.000	1200	1.000
Cyanomethyl	AN	− 2.6	0.42	− 1.485	− 1.065	− 2.452	0.086	110 000	0.289
	MA	− 2.34	0.16	− 1.336	− 1.176	− 2.709	0.067	110 000	0.289
$\pi = + 0.571$	MAN	− 2.08	0.44	− 1.188	− 0.748	− 1.722	0.179	170 000	0.447
	VA	− 0.44	− 1.56	− 0.251	− 1.811	− 4.171	0.015	13 000	0.034
	MM	− 1.18	0.23	− 0.674	− 0.444	− 1.022	0.360	240 000	0.632
	S	0	0	0.000	0.000	0.000	1.000	380 000	1.000
	VC2	− 1.34	− 0.24	− 0.765	− 1.005	− 2.315	0.099	33 000	0.087
	VEE	1.11	− 2	0.634	− 1.366	− 3.146	0.043	43 000	0.113
	AlphaMeS	− 0.04	− 0.03	− 0.023	− 0.053	− 0.122	0.885	660 000	1.737
	AC	− 2.75	0.59	− 1.570	− 0.980	− 2.258	0.105	25 000	0.066
tert-Butyl-carbonyl-methyl	AN	− 2.6	0.42	− 1.308	− 0.888	− 2.045	0.129	540 000	0.284
	MA	− 2.34	0.16	− 1.177	− 1.017	− 2.342	0.096	490 000	0.258
$\pi = + 0.503$	MAN	− 2.08	0.44	− 1.046	− 0.606	− 1.396	0.248	910 000	0.479
	VA	− 0.44	− 1.56	− 0.221	− 1.781	− 4.102	0.017	65 000	0.034
	MM	− 1.18	0.23	− 0.594	− 0.364	− 0.837	0.433	1300 000	0.684
	S	0	0	0.000	0.000	0.000	1.000	1900 000	1.000
	VC2	− 1.34	− 0.24	− 0.674	− 0.914	− 2.105	0.122	270 000	0.142
	VEE	1.11	− 2	0.558	− 1.442	− 3.320	0.036	150 000	0.079
	AlphaMeS	− 0.04	− 0.03	− 0.020	− 0.050	− 0.115	0.891	3900 000	2.053
	AC	− 2.75	0.59	− 1.383	− 0.793	− 1.827	0.161	380 000	0.200
Malonyl (II)	AN	− 2.6	0.42	− 1.256	− 0.836	− 1.925	0.146	137 000	
	MA	− 2.34	0.16	− 1.130	− 0.970	− 2.234	0.107	119 000	
$\pi = + 0.483$	AC	− 2.75	0.59	− 1.328	− 0.738	− 1.700	0.183	210 000	
Malonyl (II)	AN	− 2.6	0.42	− 2.340	− 1.920	− 4.422	0.012	137 000	
	MA	− 2.34	0.16	− 2.106	− 1.946	− 4.482	0.011	119 000	
$\pi = 0.9$	AC	− 2.75	0.59	− 2.475	− 1.885	− 4.341	0.013	210 000	
Cyanomethyl	AN	− 2.6	0.42	− 1.326	− 0.906	− 2.087	0.124		0.125
$\pi = 0.51$	S	0	0	0.000	0.000	0.000	1.000		1.000
Phenylethyl	AN	− 2.6	0.42	0.442	0.862	1.985	7.280		5
	MA	− 2.34	0.16	0.398	0.558	1.285	3.613		1.5
$\pi = - 0.17$	MM	− 1.18	0.23	0.201	0.431	0.992	2.696		1.9
	S	0	0	0.000	0.000	0.000	1.000		1
	VP-2	− 0.98	0.32	0.167	0.487	1.121	3.067		1.4
	AlphaMeS	− 0.04	− 0.03	0.007	− 0.023	− 0.053	0.948		1.1

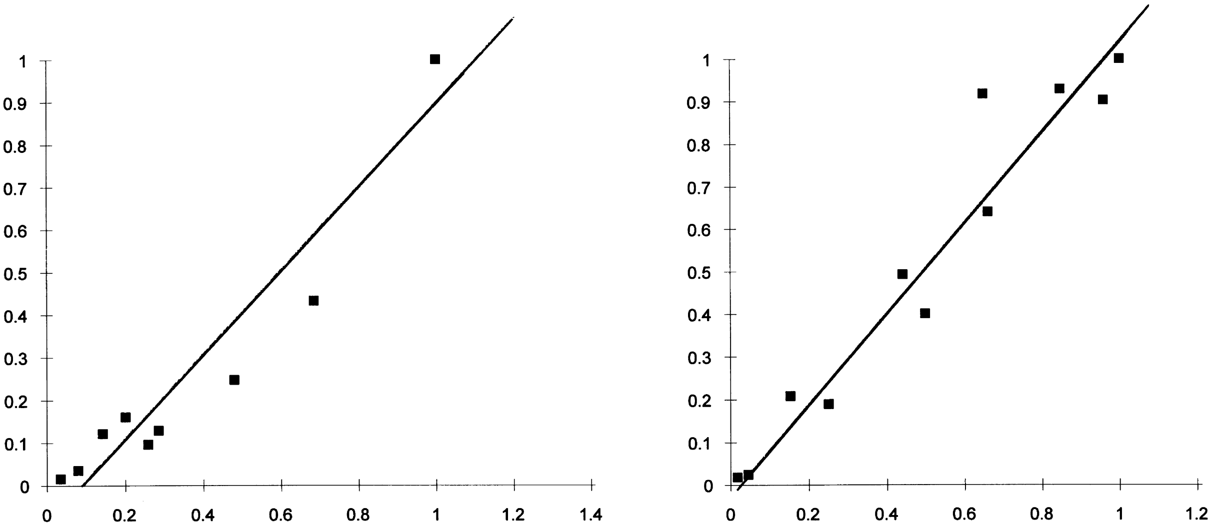
(a) Malonyl I

(b) Cyanomethyl



(c) (*tert*-Butoxy)carbonylmethyl

(d) 2-Cyano-2-propyl



(e) Benzyl

(f) Methyl

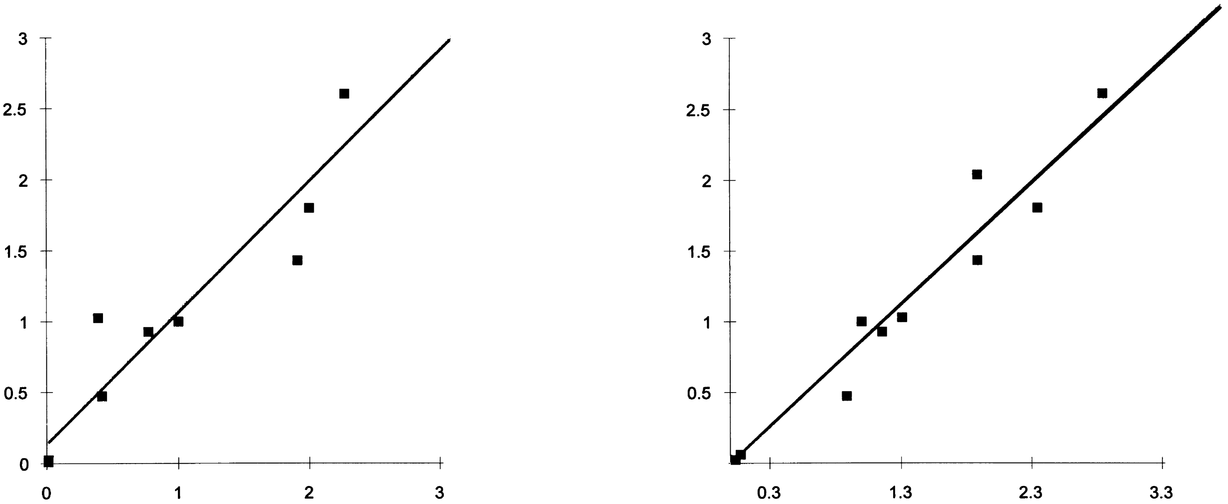
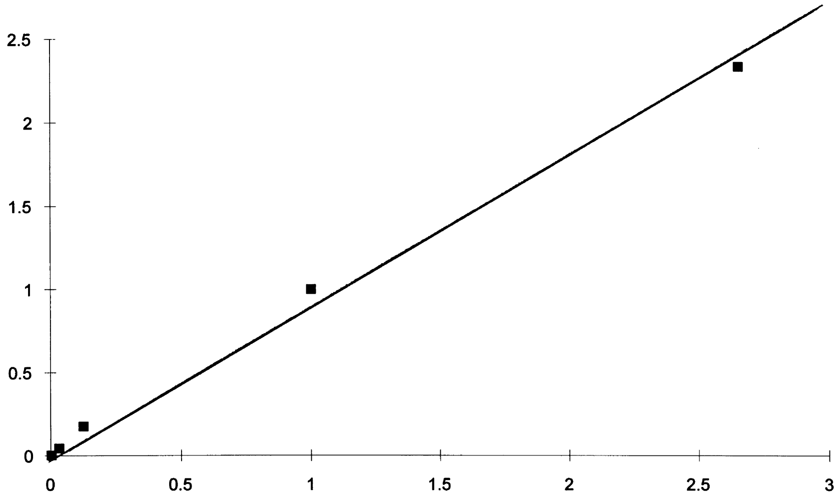


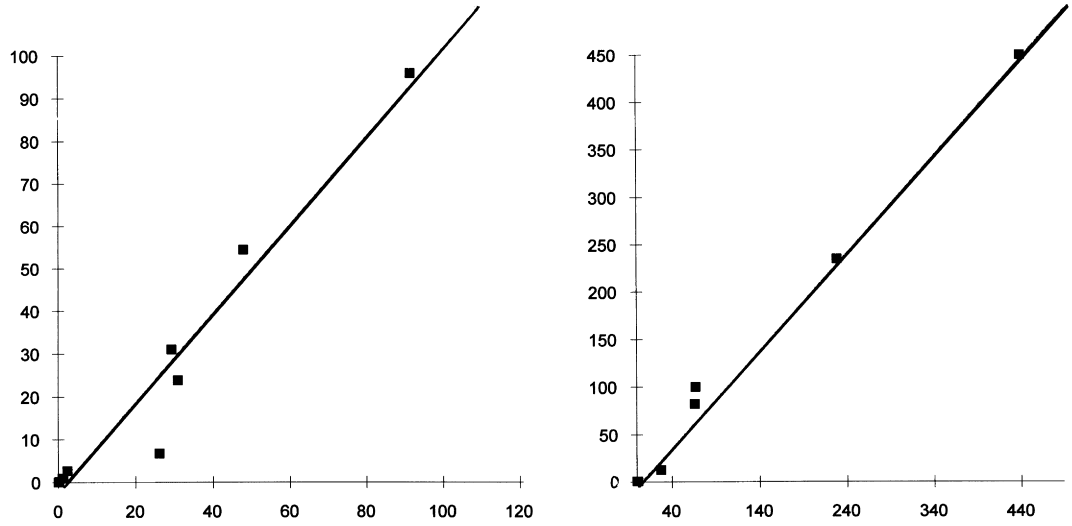
Fig. 2. Comparison of the calculated (ordinate) and experimental (abscissa) values of k_{12}/k_{13} for ten initiator radicals.

(g) *tert*-Butyl



(h) Hydroxymethyl

(i) 2-Hydroxy-2-propyl



(j) Cumyl

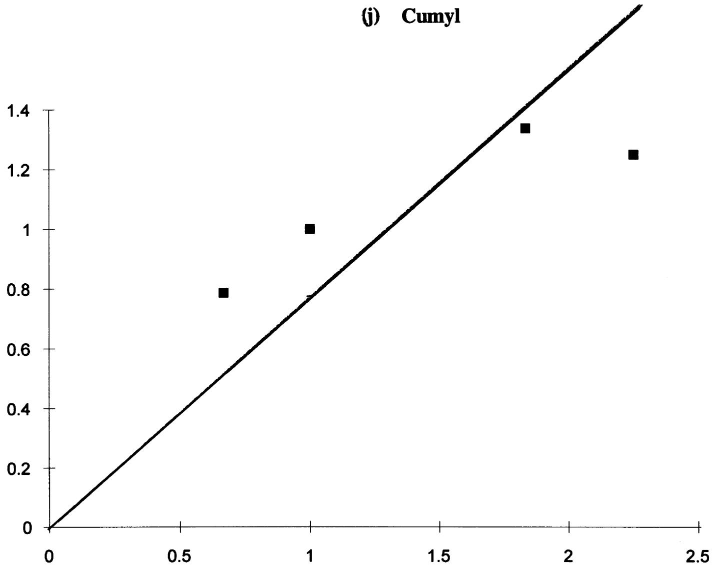


Fig. 2. (*continued*)

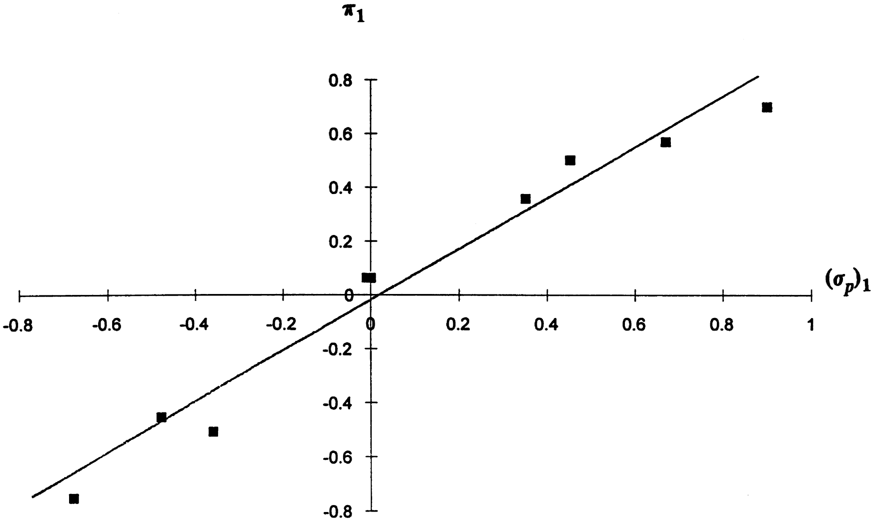


Fig. 3. Comparison of the values of π_1 and $(\sigma_p)_1$.

series of initiator radicals: benzyl [5]; (*tert*-butoxy)carbonylmethyl [6]; *tert*-butyl [7]; cumyl [5]; 2-cyano-2-propyl [8,9]; cyanomethyl [6]; 2-hydroxy-2-propyl [10–12]; hydroxymethyl [13]; malonyl I (2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl) [14]; malonyl II (di-*t*-butyl-5-malonyl) [14]; and methyl [15]. Professor Fischer has already demonstrated that his results correlate well with methyl affinities [16] and with polymerisation data [5].

In analysing all the data described in the following, the lines shown on the plots are the linear least-squares lines, generated by a computer program. In Fig. 1(a)–(j), plots of the data for the radicals are presented in descending order of π_1 value. (In every case, the abscissa represents u_2 and the ordinate $[\log(k_{12}/k_{1S}) - v_2]$.)

Of these eleven radicals, satisfactory straight lines are obtained in seven cases in plotting the data according to Eq. (11); in 2 other cases (cumyl and malonyl II), the data set consists of too few points to enable a judgment to be made. In addition, the points for the benzyl and methyl radicals are rather scattered but actually fall within a comparatively narrow range; these plots show that the π_1 value is close to zero in both cases, as would be expected considering the non-polar nature of the substituents present. The linear nature of most of these plots is strong confirmation of the basic validity of the Revised Patterns Scheme as applied to these initiating radicals.

The π_1 values determined from these plots are listed in Table 2; values for the cumyl and malonyl II radicals have been omitted for the aforementioned reason.

4. Prediction of k_{12}/k_{13} values

Once π_1 has been determined as described in the previous section, it can be used in Eq. (7), together with the necessary u, v values, to calculate k_{12}/k_{13} with the results in Table 3. Then, the predicted and experimental values of k_{12}/k_{13} can be compared graphically, as in Fig. 2(a)–(j), where the experimental values are plotted along the abscissa and the values predicted by the revised patterns scheme are along the ordinate; such a plot should have unit slope and zero intercept. The values of the slopes and intercepts obtained are given in Table 2. (The "reduced intercepts" are the actual intercepts divided by the range covered by the abscissa points, in order to add perspective.)

Almost all of these plots are satisfactorily linear, with slopes close to unity and very small intercepts, again confirming the validity of the scheme.

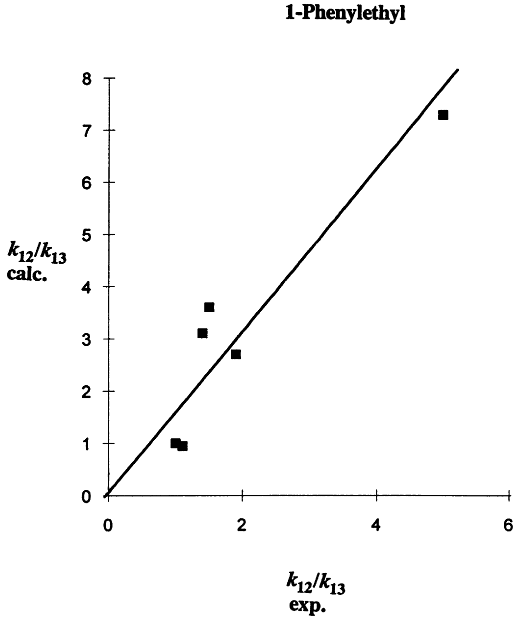


Fig. 4. Comparison of the calculated (ordinate) and experimental (abscissa) values of k_{12}/k_{13} for the 1-phenylethyl radical.

5. Discussion

At first sight it may seem that a circular argument is involved in deducing the value of π_1 from the general equation in one form and then inserting that value back in the equation in another form to predict k_{12}/k_{13}, but it is possible to validate the procedure in another way.

When the original patterns scheme [17] was advanced, the π_1 parameter had not been developed and the classic Hammett constant for a *para* substituent, the σ_p value—for the sake of consistency it will now be denoted as $(\sigma_p)_1$—was used as the measure of radical polarity, taking the algebraically-combined $(\sigma_p)_1$ values for all the substituents on the terminal carbon atom in the radical. When the revised patterns scheme was introduced [2], it was shown that the π_1 values and $(\sigma_p)_1$ values for the radicals belonging to the basic monomer set were virtually identical, and it is therefore of interest to make a similar comparison for the radicals involved in the present study. The $(\sigma_p)_1$ values obtained as before, using the data reported by Shorter [18,19], are listed in Table 2, and are plotted against the corresponding π_1 values in Fig. 3. It is readily seen that there is an excellent correlation, with a slope of 0.955, indicating near-perfect agreement. With a knowledge of the relevant $(\sigma_p)_1$ values, it would therefore be possible to predict k_{12}/k_{13} from Eq. (7) without having previously used the data to evaluate π_1. There is no objection to following this procedure where the necessary data are known but unfortunately rather few $(\sigma_p)_1$ values have been determined with the required precision.

5.1. Comments on the results for individual radicals

1. Malonyl I. The Fig. 1(a) plot is good. The Fig. 2(a) plot is the least impressive of the set because there is some scatter in points clustered near the origin. The only really unsatisfactory point is that for methyl methacrylate.
2. Cyanomethyl. Generally satisfactory, except for data for reaction with α-methyl styrene, for which the experimental k_{12}/k_{13} is about double than what would have been expected.
3. (*tert*-Butoxy)carbonylmethyl. Satisfactory, except for data for reaction with α-methyl styrene, for which the experimental k_{12}/k_{13} value is about double that expected.
4. 2-Cyano-2-propyl. Where both Bevington and Fischer have provided experimental data for the reactivity of this radical, an average value has been taken. (Their results are in good accord, especially when the temperature difference is taken into account (see the following).) The plots are entirely satisfactory.
5. Recently, data comparing the relative reactivities of this radical towards styrene and acrylonitrile have been published by Busfield, Jenkins (I.D.) and Le [20], employing a radical-trapping technique. Their results indicate that there is a surprisingly large activation energy difference for the reaction of the radical with these 2 monomers. Extrapolating their values of k_{1S}/k_{1A} of 5.3 at 105°C and 2.7 at 75°C down to 60 and 42°C, one finds the ratio to be 1.9 and 1.1, respectively, at the lower temperatures. Comparison is now possible with the results of Bevington, who obtained $k_{1S}/k_{1A} = 2.0$ at 60°C, and Heberger and Fischer, who found that $k_{1S}/k_{1A} = 1.2$ at 42°C. Clearly, the agreement between the results obtained by 3 different methods is excellent.
6. Benzyl. Very scattered points in Fig. 1(e) but a reasonable plot in Fig. 2(e), except for data for reaction with methacrylonitrile and 4-vinyl pyridine, for which the experimental k_{12}/k_{13} values are about double that expected.
7. Methyl. The points in Fig. 1(f) are scattered but the general trend is clear, however the π_1 value can only be regarded as provisional. Using a radical-trapping method, Sato and Otsu [21] determined the relative reactivity of the methyl radical towards styrene, methyl methacrylate and methacrylonitrile as 1.0: 1.82: 2.68; their points for the S/MM and S/MAN combinations fit very closely to the line in Fig. 1(f) and, in themselves, suggest that π_1 for the methyl radical is close to 0.01. Fig. 2(f) is good.
8. *tert*-Butyl. Very satisfactory.
9. Hydroxymethyl. Very satisfactory.
10. 2-Hydroxy-2-propyl. Fischer and his colleagues have published 3 papers on the reactions of this radical with somewhat different kinetic data in each case. The data in the latest of these papers [12] have been used here.
11. Cumyl. There are only four data points here, so it would be unwise to place much reliance on any analysis, especially as there is considerable scatter among the few points that we have. As one would expect a negative $(\sigma_p)_1$ value (and hence negative π_1), it may be that the least-squares line, drawn by the computer, is completely misleading.
12. Malonyl II. Only 3 experimental data points could be used. These indicate a π_1 value of 0.483, not much more that half the expected value, i.e. $(\sigma_p)_1 = 0.90$, but no conclusions can be based on so little information, and it would serve no useful purpose to plot the data.

5.2. Some additional radicals

1. Benzoyloxy. Bevington and his colleagues [8,22] have provided data on the relative reactivities of this radical with four monomers: styrene; vinyl acetate; methyl methacrylate; and acrylonitrile; the corresponding relative reactivities are: 1.0:0.36:0.12; and <0.05. If the styrene and methyl methacrylate data are used for the estimation of π_1, a value of +0.975 is obtained. Applying this result to the reactions of the remaining 2

monomers, one finds relative reactivities (relative to styrene = 1.0) for vinyl acetate and acrylonitrile of 0.01 and 0.008, respectively. The second of these figures is consistent with the reported experimental data but the first is not.

2. 1-Cyanoethyl. Prementine and Tirrell [23] found that k_A/k_S for this radical is 0.12. The $(\sigma_p)_1$ would be expected to be 0.51 and, on this basis, the revised patterns scheme predicts a value of 0.125 for this ratio, in excellent agreement with the experimental value.
3. 1-Phenylethyl. Bevington et al. [24] have provided data for this radical. Comparison of their figures with those obtained from the revised patterns scheme, using the calculated value for $(\sigma_p)_1$ of -0.17, is shown in Fig. 4, from which it can be seen that there is a reasonable qualitative correlation.
4. Phenyl. Sato and Otsu [21] determined the relative reactivity of the phenyl radical towards styrene, methyl methacrylate and methacrylonitrile as 1.0:1.78:2.46; these data suggest that π_1 for the phenyl radical is close to 0.02.
5. *tert*-Butyloxy. Sato and Otsu [21] determined the relative reactivity of this radical towards styrene, methyl methacrylate and methacrylonitrile as 1.0:0.06:0.03; these data suggest that π_1 for the radical is close to 1.0. Thus, the values of π_1 for the 2 cases where the unpaired electron is borne on oxygen (benzoyloxy and *tert*-butyloxy) are almost identical.
6. Benzothiyl. Sato, Mabe and Otsu [25] determined the relative reactivity of this radical towards styrene and methyl methacrylate as 1.0:0.12. This slim evidence corresponds to a π_1 value close to 1.0, virtually identical to the value for oxygen-borne radicals.

6. Conclusions

The extension of the Revised Patterns Scheme to the case of initiator radicals has proved to be both simple and successful. The π_1 values so-derived are in all cases very close to the $(\sigma_p)_1$ values where sufficient knowledge exists to evaluate the latter quantity. Ratios of rate constants for the addition to competing monomers of a total of 17 initiator radicals, deduced from the scheme, are in good agreement with experimental results in the literature.

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