

# Non-classical free-radical polymerization.

## 6. Degradative addition in the polymerization of acenaphthylene: a treatment including size-dependent termination coefficients

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The structure of acenaphthylene suggests that degradative addition to monomer may occur during free-radical polymerization. We present an analysis, based on the kinetic treatment in an earlier paper, of the kinetic data of Romani and Weale<sup>1</sup> on the polymerization of acenaphthylene in toluene at 1 atm pressure. Two cases are considered: (i) where the termination coefficient is constant, and (ii) where  $k_t$  is size-dependent. The latter case is appropriate because small radicals are involved; analysis is facilitated by introduction of the concept of a 'group-termination-coefficient'. Both treatments lead to results in good agreement with the experimental data, which are, therefore, consistent with the occurrence of degradative addition in this polymerization. The estimated kinetic parameters have different values in (i) and (ii), notably in that re-initiation is important in the latter, but insignificant in the former. Possible techniques for more detailed examination of re-initiation are outlined. Molecular weight distributions for the polymerization with degradative addition to monomer with constant  $k_t$  have been calculated.

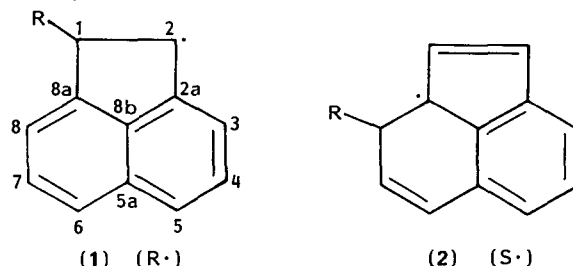
(Keywords: free-radical polymerization; degradative addition; size-dependent termination coefficient; group-termination concept; acenaphthylene structure)

### INTRODUCTION

Although the free-radical polymerization of acenaphthylene has been known for many years the kinetic aspects have received relatively little attention. Romani and Weale<sup>1</sup> made a careful study of the reactions in toluene and carbon tetrachloride solutions at 60°C with initiation by azobisisobutyronitrile under pressures of 1, 1400 and 2800 atmospheres. They reported that the kinetic behaviour deviated from classical; the initiator and monomer exponents were approximately 0.62 and 0.84, respectively in toluene at 1 atmosphere. This behaviour was attributed to degradative transfer to monomer, but no details were given. In the present paper we consider the data of Romani and Weale for the polymerization in toluene under a pressure of 1 atmosphere and endeavour to show that they are consistent with the occurrence of degradative addition to monomer.

Degradative addition, in its simplest form, involves retardation by monomer arising from addition of the latter to propagating radicals with formation of a distinct radical species of lower reactivity which enters into normal termination reactions but does not necessarily re-initiate<sup>2,3</sup>. Kinetic features associated with this type of polymerization have been discussed in an earlier paper<sup>4</sup>.

For present purposes two properties of acenaphthylene merit consideration. First, the five-membered ring in the molecule has significant steric strain which is relieved when polymerization occurs through the double bonds in the 5-membered rings, giving rise to an unusually high heat of polymerization<sup>5-7</sup>. Hence one might expect that a radical such as (1) formed by addition to C<sub>1</sub>, would be delocalized only to a relatively small extent. Similarly it seems unlikely that addition to an aromatic ring, e.g. as in (2) would produce a radical showing much delocalization into the five-membered ring, although it might be delocalized otherwise. Molecular orbital calculations confirm and quantify these simple ideas. They show that radical addition in general is favoured over hydrogen abstraction and reveal many sites of comparable reactivity towards an attacking radical.



Further, they confirm that radical (2) is much less reactive in monomer addition than (1). Some results of the calculations are presented in Appendix 2.

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The behaviour of some aromatic molecules as inhibitors of radical chain reactions is indeed well-known. Kooyman and Farenhorst<sup>8</sup> studied inhibition of the chain-addition of carbon tetrachloride to olefins<sup>9</sup> and Bagdasar'ian and his colleagues<sup>10</sup> demonstrated experimentally that active radicals prefer to add to aromatic systems rather than abstract hydrogen, producing radicals of low reactivity. These latter authors evaluated rate coefficients for inhibition of some free-radical polymerizations by aromatic compounds.

Occurrence of degradative addition in the polymerization of acenaphthylene would, therefore, not be surprising. For consistency with our earlier paper<sup>4</sup> we shall designate the reactive radicals, formed by addition at C<sub>1</sub> or C<sub>2</sub> by R· (cf. 1) and the relatively inactive radicals, arising from addition elsewhere, by S· (2).

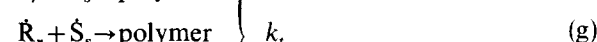
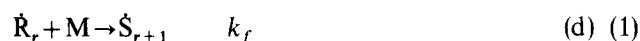
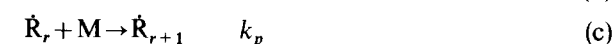
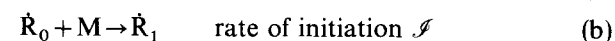
The second characteristic of acenaphthylene which must be borne in mind is the very crowded nature of the polymer. Story and Canty<sup>11</sup> studied models of the polymers and also characterized polyacenaphthylene prepared by ionic polymerization. They proposed the formation of iso- and syndio-tactic structures, the former rod-like and the latter helical. Some structures could not be constructed and so the possibility of self-termination arises. In principle, it is possible for (radical) propagation to occur until a radical is formed which is unfavourably situated for 'normal' propagation. Such a radical might constitute a pseudo-S· radical allowing limited termination and re-initiation. It would thus seem feasible to devise a mechanism for degradative addition based on physical factors related to radical occlusion instead of inherent differences in radical reactivity. While this cannot be discounted for acenaphthylene polymerization we believe the former mechanism is more likely in view of the kinetic discussion below.

It is generally believed that the mean bimolecular termination coefficient in free-radical polymerization, although sensibly constant for large radical sizes, shows a significant size-dependence for 'small' radicals (typically those with fewer than ~100 units), with consequent complications of the interpretation of kinetic data<sup>12</sup>. Many retarded polymerizations would be expected to show complications of this kind, including those studied by Romani and Weale<sup>1</sup> which are the subject of this paper. Unfortunately, degrees of polymerization were not reported by these authors for conditions corresponding to those holding in the kinetic runs, but simple considerations show that the mean radical sizes lay between 20 and 200, i.e. in the range in which the termination coefficient is usually size-dependent. Under these conditions, therefore, the polymerization of acenaphthylene is doubly non-classical.

## GENERAL TREATMENT

### Kinetics of degradative addition

The kinetic scheme we have used in the earlier paper<sup>4</sup> is presented in equation (1) in which the symbols have their conventional meanings. In kinetic expressions throughout we have omitted brackets from concentration terms for clarity.



Conventional stationary-state treatment, with the long-chain assumption, gives for the rate of polymerization  $\omega$

$$\omega = k_p M \left( \frac{\mathcal{I}}{k_t} \right)^{1/2} \frac{k_{pm} M + (\mathcal{I} k_t)^{1/2}}{(k_{pm} + k_f) M + (\mathcal{I} k_t)^{1/2}} \quad (2)$$

in which  $\mathcal{I}$  is the rate of initiation.

Equation (2) may be recast into the forms (3) and (4), which are useful for plotting experimental data<sup>4</sup>

$$\frac{M \cdot \mathcal{I}^{1/2}}{\omega} \left\{ 1 + \frac{k_{pm} M}{(\mathcal{I} k_t)^{1/2}} \right\} = \frac{k_t^{1/2}}{k_p} \left\{ 1 + \frac{k_f + k_{pm} M}{(\mathcal{I} k_t)^{1/2}} \right\} \quad (3)$$

$$\left( \frac{M \cdot \mathcal{I}^{1/2}}{\omega} - \frac{k_t^{1/2}}{k_p} \right)^{-1} = \frac{k_p}{k_f} \left\{ \frac{\mathcal{I}^{1/2}}{M} + \frac{k_{pm}}{k_t^{1/2}} \right\} \quad (4)$$

It is now necessary to consider how expressions (2), (3), (4), may be modified to include size-dependent termination.

*Radical-size-dependent  $k_t$ : the 'group-termination coefficient'*

A number of attempts have been made<sup>13</sup> to establish a theoretical form of the dependence of  $k_t$  on radical size based on diffusion control of the reaction. Clearly an expression suitable for use in kinetic schemes is particularly desirable and proposals have been advanced<sup>14-27</sup>, some based on semi-empirical or numerical<sup>23</sup> approaches.

A simple power-law approximation

$$k_t = k(\overline{xy})^{-b} \quad (5)$$

where  $\overline{xy}$  is a mean of the two radical sizes  $x, y$  and  $k$  is a constant used by Yasukawa, Takabashi and Murakami<sup>17</sup> and by Yasukawa and Murakami<sup>19</sup> and has received considerable attention. The geometric mean leads to the simplest calculations<sup>26</sup> because it gives rise to factorizable expressions, but on physical grounds the harmonic mean appears to be the most appropriate simple average<sup>23</sup>. Olaj and Zifferer<sup>27</sup> have derived some universal relationships for arbitrary chain-length dependence of  $k_t$ .

In this paper we introduce a 'group termination coefficient' concept, according to which, as far as the termination coefficient is concerned, a group of radicals behaves as a single radical of size  $\bar{r}$ , the number average for the group. The group termination coefficient is supposed to be proportional to  $\bar{r}^{-2\beta}$ ,  $\beta$  being a positive exponent, and may be written as

$$k_t = k_{t_0} \left( \frac{\bar{r}}{r_0} \right)^{-2\beta} \quad (6)$$

where  $k_{t_0}$  is the termination coefficient for radicals of an arbitrarily chosen size  $r_0$ . The rate of termination in a free-

radical polymerization is then given by expression (7)

$$k_{t_0} \left( \frac{\bar{r}}{r_0} \right)^{-2\beta} \left( \sum_r \mathbf{R}_r \right)^2 \quad (7)$$

where  $\mathbf{R}_r$  is the concentration of radicals of size  $r$ . This is clearly an approximation for the more usual type of expression based on the geometric mean, according to which the rate of termination may be expressed in the form

$$\frac{k_{t_0}}{r_0^{-2\beta}} \left( \sum_r r^{-\beta} \mathbf{R}_r \right)^2 \quad (8)$$

Its use, involving the replacement of  $\sum_r r^{-\beta} \mathbf{R}_r$  by  $\bar{r}^{-\beta} \sum_r \mathbf{R}_r$ , introduces some error which, however, is not very significant for values of  $\beta$  generally encountered. For example, if  $\mathbf{R}_r$  has a simple exponential distribution and  $\bar{r} \gg 1$  we find

$$\frac{\sum_r r^{-\beta} \mathbf{R}_r}{\bar{r}^{-\beta} \sum_r \mathbf{R}_r} = \Gamma(1-\beta) \quad (9)$$

independent of  $\bar{r}$ . A more realistic radical distribution for a system with variable  $k_t$ , holding for second-order termination in the absence of chain transfer, is shown in equation (10) in which  $A$  and  $\mu$  are constants.

$$\mathbf{R}_r = A \exp(-\mu r^{1-\beta}) \quad (10)$$

For this distribution

$$\frac{\sum_r r^{-\beta} \mathbf{R}_r}{\bar{r}^{-\beta} \sum_r \mathbf{R}_r} = \frac{[\Gamma\{2/(1-\beta)\}]^\beta}{[\Gamma\{1/(1-\beta)\}]^{1+\beta}} \quad (11)$$

again independent of  $\bar{r}$ .

For reasons outlined below we have used the (rather large) value  $\beta=0.16$ . Olaj and his colleagues<sup>23,26,27</sup> have favoured  $\beta=0.08$ . The ratios in equations (9) and (11) are equal to 1.122 and 1.137, respectively for  $\beta=0.16$ , and to 1.053 and 1.056, respectively for  $\beta=0.08$ . Note that for  $\beta=0$  termination is classical with constant  $k_t$  and both expressions (9) and (11) reduce to unity. Use of the simple group termination coefficient thus introduces errors which become more significant as  $\beta$  increases. These errors are readily eliminated by inclusion of factors such as that in equation (11) during the development<sup>29</sup>. We are of the opinion that it does not distort the kinetic relationships significantly although it may influence the parameters. This question is taken up again later.

#### Application to kinetic scheme

In developing expression (2) from the kinetic scheme (1) we find that  $k_t$  enters into three terms

$$k_t \left( \sum_r \mathbf{R}_r \right)^2, \quad k_t \sum_r \mathbf{R}_r \sum_s \mathbf{S}_s \quad \text{and} \quad k_t \left( \sum_s \mathbf{S}_s \right)^2 \quad (12)$$

(According to the arguments presented in our earlier paper<sup>4</sup>, in degradative addition  $k_t$  may be considered independent of the chemical natures of the radicals

involved.) If  $k_t$  has a geometric-mean type of size dependence, the terms in (12) must be replaced by those in (13) in which  $k_{t_0}$  is the

$$k_{t_0} \left\{ \sum_r \left( \frac{r}{r_0} \right)^{-\beta} \mathbf{R}_r \right\}^2$$

$$k_{t_0} \left\{ \sum_r \left( \frac{r}{r_0} \right)^{-\beta} \mathbf{R}_r \right\} \left\{ \sum_s \left( \frac{s}{s_0} \right)^{-\beta} \mathbf{S}_s \right\}$$

$$k_{t_0} \left\{ \sum_s \left( \frac{s}{s_0} \right)^{-\beta} \mathbf{S}_s \right\}^2 \quad (13)$$

termination coefficient for radicals of an arbitrarily chosen size  $r_0 (=s_0)$ . With the aid of our group-termination assumption (equation 6) these expressions become

$$k_{t_0} \left( \frac{\bar{r}}{r_0} \right)^{-2\beta} \dot{\mathbf{R}}^2 \quad k_{t_0} \left( \frac{\bar{r}}{r_0} \right)^{-\beta} \left( \frac{\bar{s}}{s_0} \right)^{-\beta} \dot{\mathbf{R}} \dot{\mathbf{S}} \quad k_{t_0} \left( \frac{\bar{s}}{s_0} \right)^{-2\beta} \dot{\mathbf{S}}^2 \quad (14)$$

respectively, where  $\dot{\mathbf{R}} = \sum_r \mathbf{R}_r$ ,  $\dot{\mathbf{S}} = \sum_s \mathbf{S}_s$ . From Appendix (1)

we see that, for constant  $k_t$ ,  $\bar{r} = \bar{s}$  and we assume that this holds (at least approximately) under present conditions. It follows that by making the substitution for  $k_t$  shown in equation (6) we can apply equation (2) when  $k_t$  is size dependent. For this purpose it is convenient to define a factor  $F(\bar{r})$  as in equation (15)

$$\left( \frac{k_t}{k_{t_0}} \right)^{1/2} = F^{-1}(\bar{r}) \quad (15)$$

or

$$F(\bar{r}) = \left( \frac{\bar{r}}{r_0} \right)^\beta$$

(from equation (6)).

We thus obtain equations (16), (17) and (18) from equations (2), (3) and (4).

$$\omega = k_p FM \left( \frac{\mathcal{J}}{k_{t_0}} \right)^{1/2} \frac{k_{pm} FM + (\mathcal{J} k_{t_0})^{1/2}}{(k_{pm} + k_f) FM + (\mathcal{J} k_{t_0})^{1/2}} \quad (16)$$

$$\frac{FM \mathcal{J}^{1/2}}{\omega} \left\{ 1 + \frac{k_{pm} FM}{(\mathcal{J} k_{t_0})^{1/2}} \right\} = \frac{k_{t_0}^{1/2}}{k_p} \left\{ 1 + \frac{(k_f + k_{pm}) FM}{(\mathcal{J} k_{t_0})^{1/2}} \right\} \quad (17)$$

$$\left( \frac{FM \mathcal{J}^{1/2}}{\omega} - \frac{k_{t_0}^{1/2}}{k_p} \right)^{-1} = \frac{k_p}{k_f} \left\{ \frac{\mathcal{J}^{1/2}}{FM} + \frac{k_{pm}}{k_{t_0}^{1/2}} \right\} \quad (18)$$

According to equation (17) a plot of  $FM \mathcal{J}^{1/2}/\omega$  versus  $FM/\mathcal{J}^{1/2}$  has an intercept  $k_{t_0}^{1/2}/k_p$  on the  $FM \mathcal{J}^{1/2}/\omega$  axis, so that if measurements of  $\omega$  down to low values of  $M/\mathcal{J}^{1/2}$  are available, or if  $k_{pm}$  is small (as is usually the case)  $k_{t_0}^{1/2}/k_p$  may thus be evaluated, at least approximately. The value may be refined when  $k_{pm}/(\mathcal{J} k_{t_0})^{1/2}$  becomes known. For this purpose the left side of equation (18) is plotted against  $\mathcal{J}^{1/2}/FM$  to give a straight line having

$$\text{slope} = k_p/k_f \quad \text{intercept} = \frac{k_p k_{pm}}{k_f k_{t_0}^{1/2}} \quad (19)$$

Hence from equations (17)–(19) the three parameters  $k_p/k_{t_0}^{1/2}$ ,  $k_f/k_p$  and  $k_{pm}/k_p$ , or their equivalents, may be

determined. Equation (19) obviously holds also for constant  $k_t$  ( $F=1$ ).

#### Numerical values

In this paper we suppose that  $k_t=k_{t_0}$  for an arbitrary standard radical size  $r_0=50$  and  $\beta=0.16$ . This latter is consistent with a linear extrapolation to radical sizes below 100 of the experimental data of O'Driscoll and Mahabadi in their plot of  $k_t$  versus  $\log(\text{radical size})$  for poly(methyl methacrylate) radicals<sup>28</sup>. The value  $\beta=0.16$ , corresponding to  $b=0.32$  in the nomenclature of Olaj and colleagues<sup>26,27</sup>, is larger than any used by the latter authors, but we wished to employ an extreme value to examine the effects on the kinetic behaviour.

We have found<sup>29</sup> that  $\bar{r}$ , which is necessary for evaluating  $F(\bar{r})$  from equation (15), may be calculated to a sufficiently good approximation from the relation (20)

$$\bar{r} = \frac{\omega}{\mathcal{I} + \omega C_x X/M} \left[ (1-\beta) \frac{\Gamma 2/(1-\beta)}{\{\Gamma 1/(1-\beta)\}^2} \right] \quad (20)$$

in which  $X$  represents a non-degradative transfer constant  $C_x$ . More accurately,  $\beta$  in equation (20) should be replaced by a more complicated function  $u$ . Thus

$$u \sim \frac{a}{\sigma} \frac{C_m(\sigma-a) + \sigma^2}{\sigma C_x X/M + a(\sigma + C_m)} \beta \quad (a)$$

(21)

$$\text{where } a = \frac{(\mathcal{I} k_{t_0})^{1/2}}{k_p M} r_0^\beta; \quad \sigma = \frac{k_{pm}}{k_p} + a \quad (b)$$

$C_m = k_f/k_p$  is the degradative 'transfer' constant for the monomer. The errors introduced by use of the simple relation (20) are not significant for the present purposes. These matters will be discussed in a future publication<sup>29</sup>.

To examine the possible errors introduced we have calculated  $F$  in two other ways: (i)  $F(\bar{P}_0/2)$  from equation (15) with  $\bar{r}$  replaced by  $\bar{P}_0/2$  ( $\bar{P}_0 = 2\omega/\mathcal{I}$  is the number-average degree of polymerization in the absence of transfer) and (ii)  $F(\bar{P}_n/2)$  from equation (15) with  $\bar{r}$  replaced by  $\bar{P}_n/2$ , where  $\bar{P}_n$  is the number-average degree of polymerization in the presence of transfer, calculated from  $\bar{P}_0$  by use of the Mayo equation (Appendix 1,

equation (38). We have assumed that termination occurs predominantly by radical combination.  $F(\bar{P}_n/2)$  is approximately 5% smaller than the corresponding  $F(\bar{r})$ . As expected,  $F(\bar{r})$  is not very sensitive to small changes in  $\bar{r}$ . In polymerizations with constant  $k_t$ , in the absence of transfer, the ratio  $\bar{r}/\bar{P}_n$  is determined simply by the ratio combination:disproportionation in the termination reaction, but when  $k_t$  has a size-dependence of the form discussed the ratio is also a function of  $\beta$  and is somewhat larger than with constant  $k_t$ . Nevertheless approximate proportionality between  $\bar{r}$  and  $\bar{P}_n$  remains, even in the presence of moderate chain-transfer, as suggested by the data in Table 1.

## RESULTS AND DISCUSSION

We have taken the first order coefficient for decomposition of azobisisobutyronitrile (3) in toluene at 60°C to be  $1.2 \times 10^{-5} \text{ s}^{-1}$  and assumed the efficiency of initiation to have the conventional value 0.54 (cf. ref. 2). The rate of initiation is then given by equation (22).

$$\mathcal{I} = 1.3 \times 10^{-5} [(3)] \text{ mol dm}^{-3} \text{ s}^{-1} \quad (22)$$

Table 1 presents the experimental data<sup>1</sup> for  $M$ ,  $\omega$  and  $C_x X/M$  together with calculated values of  $\mathcal{I}$ ,  $\bar{r}$  (equation 20),  $\bar{P}_0$ ,  $\bar{P}_n$ ,  $F(\bar{r})$ ,  $F(\bar{P}_0/2)$ ,  $F(\bar{P}_n/2)$ . Romani and Weale's value<sup>1</sup> for the transfer-constant of toluene  $C_x = 6.8 \times 10^{-4}$  has been used. Uncertainties in this quantity have only a small influence on the calculations.

Straight-line plots presented in the figures are least-square regression lines. Since errors introduced into plots based on equations (4) and (18) are disproportionately large when the two terms on the left have similar values, such plots include only 10 out of the 15 data points, corresponding to the largest 10 values of  $M\mathcal{I}^{1/2}/\omega$  or  $FM\mathcal{I}^{1/2}/\omega$ . This will be illustrated later.

#### Constant termination coefficient

A plot of  $M\mathcal{I}^{1/2}/\omega$  versus  $M/\mathcal{I}^{1/2}$  is given in Figure 1, and shows that equation (3) is obeyed with  $k_{pm}M/(\mathcal{I}k_t)^{1/2} \ll 1$ , i.e. with  $k_{pm}$  very small. This is consistent with Figure 2 in which the left side of equation (4) is plotted against  $\mathcal{I}^{1/2}/M$ . The least squares line passes close to the origin indicating that  $k_{pm} \sim 0$  (cf. equation 19).

Table 1 Experimental data and derived quantities (60°C)

$M$ (mol dm <sup>-3</sup> )	$10^7 \mathcal{I}$ (mol dm <sup>-3</sup> s <sup>-1</sup> )	$10^6 \omega$ (mol dm <sup>-3</sup> s <sup>-1</sup> )	$10^3 C_x X/M$	$\bar{r}$	$\bar{P}_0$	$\bar{P}_n$	$F(\bar{r})$	$F(\bar{P}_0/2)$	$F(\bar{P}_n/2)$
0.50	1.814	2.99	11.7	16.8	33.0	23.8	0.8399	0.8371	0.7949
0.75	1.814	4.54	7.446	25.7	50.1	36.5	0.8990	0.8953	0.8512
1.00	1.814	5.48	5.311	31.7	60.4	45.7	0.9297	0.9225	0.8824
1.20	1.814	7.33	4.243	41.9	80.8	60.2	0.9721	0.9665	0.9221
1.50	1.814	7.98	3.182	46.9	88.0	68.7	0.9898	0.9798	0.9418
2.00	1.814	10.40	2.115	62.2	114.7	92.3	1.0356	1.0222	0.9874
2.50	1.814	12.80	1.476	77.7	141.1	116.8	1.0731	1.0566	1.0253
3.00	1.814	14.50	1.047	89.7	159.9	137.0	1.0980	1.0780	1.0518
2.00	0.241	2.91	2.115	117.0	241.5	159.9	1.1457	1.1515	1.0782
2.00	0.482	4.55	2.115	95.7	188.8	134.9	1.1095	1.1070	1.0492
2.00	0.723	5.80	2.115	83.4	160.4	119.8	1.0853	1.0785	1.0295
2.00	0.964	6.93	2.115	75.9	143.8	110.3	1.0691	1.0598	1.0160
2.00	1.203	7.94	2.115	70.4	132.0	103.2	1.0563	1.0452	1.0052
2.00	1.685	9.89	2.115	63.5	117.4	94.0	1.0390	1.0260	0.9903
2.00	2.411	12.30	2.115	56.0	102.0	83.9	1.0183	1.0032	0.9725

The kinetic parameters evaluated from Figures 1 and 2 with the aid of equations (3), (4) and (19) are given in Table 2. Using these we may calculate the  $\omega$ - $M$  relation (constant  $\mathcal{J}$ ) and  $\omega$ - $\mathcal{J}$  relation (constant  $M$ ) from equation (2). These are presented in Figures 3 and 4 which show very good agreement between observed and calculated values. This latter is to be expected, since the data are fitted closely by equations (3) and (4), which are equivalent to equation (2).

#### Size-dependent termination coefficient

Figure 5 shows that a plot of  $F(\bar{r})M\mathcal{J}^{1/2}/\omega$  versus  $F(\bar{r})/\mathcal{J}^{1/2}$  (equation 17) for the data in Table 1 has a

distinct curvature, as would be anticipated if the term  $k_{pm}F(\bar{r})M/(\mathcal{J}k_{t_0})^{1/2}$  on the left of equation (17) were not negligible. The intercept on the ordinate ( $k_{t_0}^{1/2}/k_p$ ) is approximately  $50 \text{ mol}^{1/2} \text{ dm}^{-3/2} \text{ s}^{1/2}$ . We have obtained consistent results by taking this intercept as  $49.0 \text{ mol}^{1/2} \text{ dm}^{-3/2} \text{ s}^{1/2}$ . In general, evaluation of the precise value of  $k_{t_0}^{1/2}/k_p$  involves iteration. The first value from equation (17) is used in equation (18) to obtain  $k_{pm}/k_{t_0}^{1/2}$ . This is then inserted into equation (17) and the latter plotted to obtain an improved value of  $k_{t_0}^{1/2}/k_p$ . The process is repeated until a satisfactory degree of

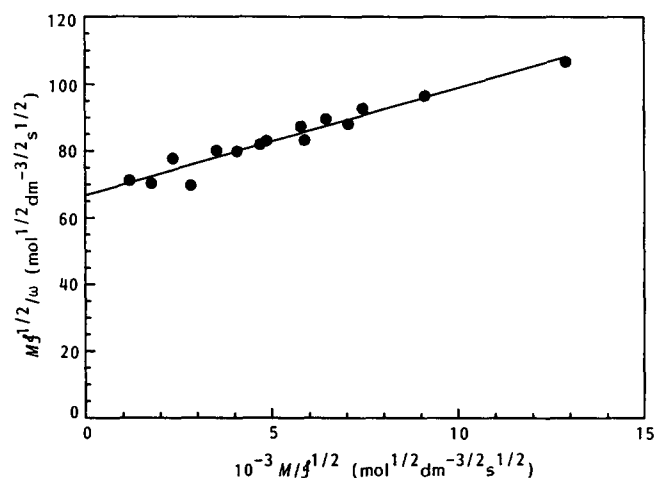


Figure 1 Plot of  $M\mathcal{J}^{1/2}/\omega$  vs.  $M/\mathcal{J}^{1/2}$  (cf. equation (3)) for data in Table 1

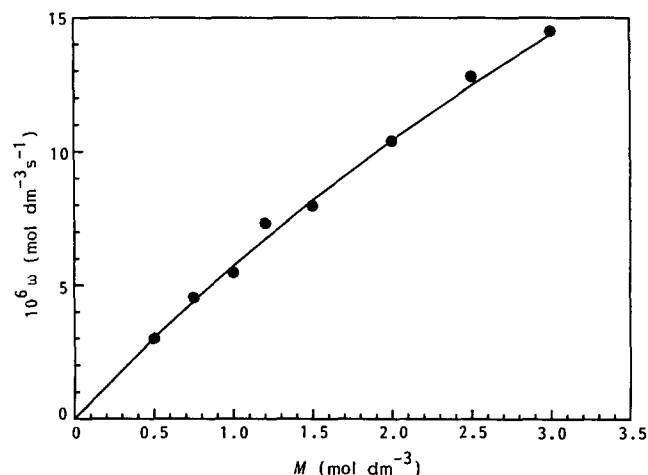


Figure 3  $\omega$ - $M$  relation for  $\mathcal{J} = 1.814 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$  calculated from equation (2) with parameters in Table 2 (constant  $k_t$ ): experimental points

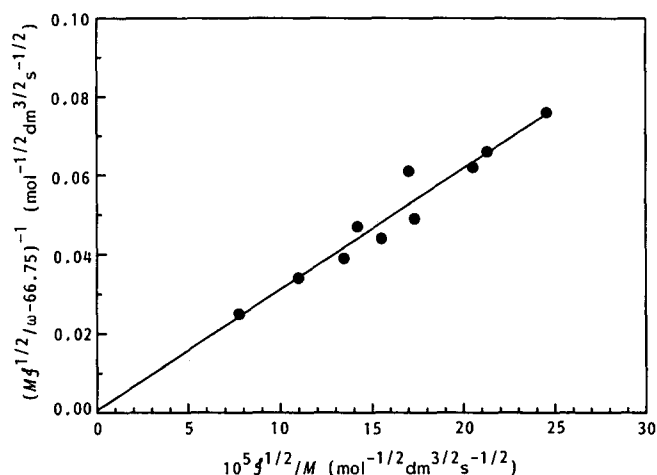


Figure 2 Plot of data in Table 1 according to equation (4). Only 10 data points (those with the largest 10 values of  $M\mathcal{J}^{1/2}/\omega$ ) are included (see text)

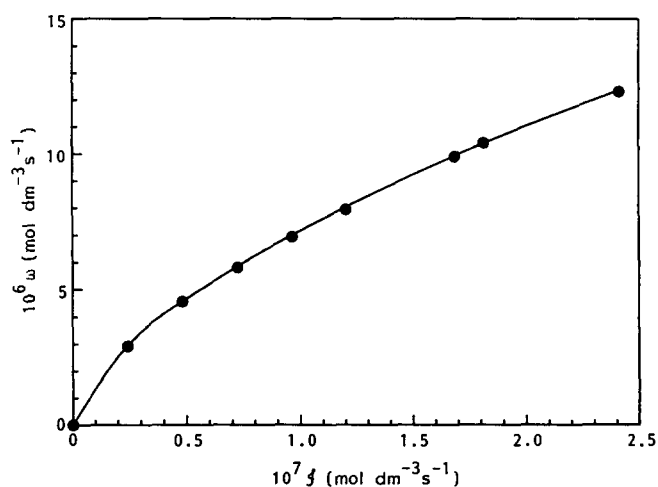


Figure 4  $\omega$ - $\mathcal{J}$  relation for  $M = 2.0 \text{ mol dm}^{-3}$  calculated from equation (2) with parameters in Table 2 (constant  $k_t$ ): experimental points

Table 2 Kinetic parameters (60°C)

Parameter/kinetic procedures	From $F(\bar{r})$	From $F(\bar{P}_0/2)$	From $F(\bar{P}_n/2)$	Constant $k_t$
$10^2 \frac{k_p}{k_{t_0}^{1/2}}$ (or $10^2 \frac{k_p}{k_{t_0}^{1/2}}$ ) ( $\text{mol}^{-1/2} \text{ dm}^{3/2} \text{ s}^{-1/2}$ )	2.0	2.0	2.2	1.5
$10^3 \frac{k_f}{k_p}$	10.1	9.1	11.1	3.3
$10^4 \frac{k_f}{k_{t_0}^{1/2}}$ (or $10^4 \frac{k_f}{k_{t_0}^{1/2}}$ ) ( $\text{mol}^{-1/2} \text{ dm}^{3/2} \text{ s}^{-1/2}$ )	2.1	1.8	2.5	0.49
$10^3 \frac{k_{pm}}{k_p}$	3.6	3.1	4.1	0.13
$10^5 \frac{k_{pm}}{k_{t_0}^{1/2}}$ (or $10^5 \frac{k_{pm}}{k_{t_0}^{1/2}}$ ) ( $\text{mol}^{-1/2} \text{ dm}^{3/2} \text{ s}^{-1/2}$ )	7.2	6.2	9.1	0.20

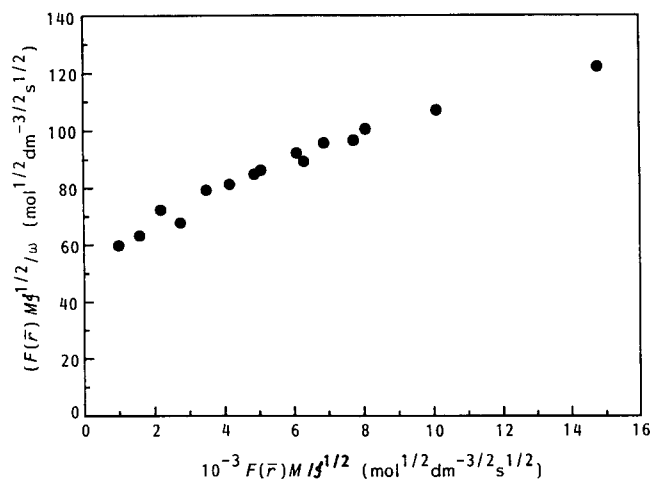


Figure 5 Plot of  $F(\bar{r})Mf^{1/2}/\omega$  versus  $F(\bar{r})Mf^{1/2}$  (cf. equation (17)) for data in Table 1

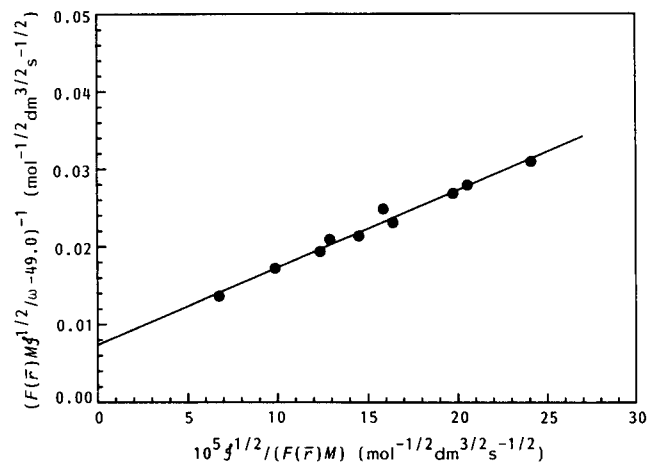


Figure 6 Plot of data in Table 1 according to equation (18) ( $F \equiv F(\bar{r})$ ). Only 10 data points (those with the largest 10 values of  $Mf^{1/2}/\omega$ ) are included (see text)

consistency between the two equations (and a stationary value of  $k_{t_0}^{1/2}/k_p$ ) (Figures 6 and 7) is obtained. The resulting kinetic parameters, and also those based on  $F(\bar{P}_n/2)$  and  $F(\bar{P}_0/2)$  evaluated similarly, are presented in Table 2.

Figures 8 and 9 indicate that the  $\omega$ - $M$  and  $\omega$ - $f$  curves (equation 16) calculated from the  $F(\bar{r})$  parameters agree well with the experimental observations. This is also true for the other sets of parameters in Table 2.

Figure 10 is included to illustrate the sensitivity of equations (4) and (18) to experimental errors in  $\omega$ . The three 'wild' points in this figure may be identified in the  $\omega$ - $M$  curve in Figure 8 at  $M=0.50, 1.0, 1.2 \text{ mol dm}^{-3}$ . The highest point in Figure 10 ( $M=0.50$ ) would fall on the line if  $\omega$  were increased by 3.3%, a discrepancy hardly significant in Figure 8. The amplification of errors in Figure 10 is thus evident. The dotted line is the regression line based on all fifteen points. We believe it is less accurate.

If, for a given set of  $r$  values,  $F(\bar{r})$  is multiplied by a factor  $f$ , we see from inspection of equations (16)–(18) that the derived values of the parameters  $k_p/k_{t_0}^{1/2}$ ,  $k_f/k_{t_0}^{1/2}$  and  $k_{pm}/k_{t_0}^{1/2}$  are proportional to  $1/f$ , while  $k_f/k_p$  and  $k_{pm}/k_p$  are invariant. It follows from our earlier discussion that simple use of the group termination coefficient as described produces errors which may be regarded as equivalent to the introduction of a factor into  $F$ , at least

for the two examples referred to in equations (9) and (11). Thus when equation (6) applies the errors in  $k_p/k_{t_0}^{1/2}$ ,  $k_f/k_{t_0}^{1/2}$  and  $k_{pm}/k_{t_0}^{1/2}$  arising in this way would be approximately 14%. Similar changes would result from changing the standard radical size from 50 to approximately 115.

According to Table 1  $F(\bar{r}) > F(\bar{P}_0/2) > F(\bar{P}_n/2)$  and from the above remarks we might expect each of the derived parameters  $k_p/k_{t_0}^{1/2}$ ,  $k_f/k_{t_0}^{1/2}$  to have values in the reverse

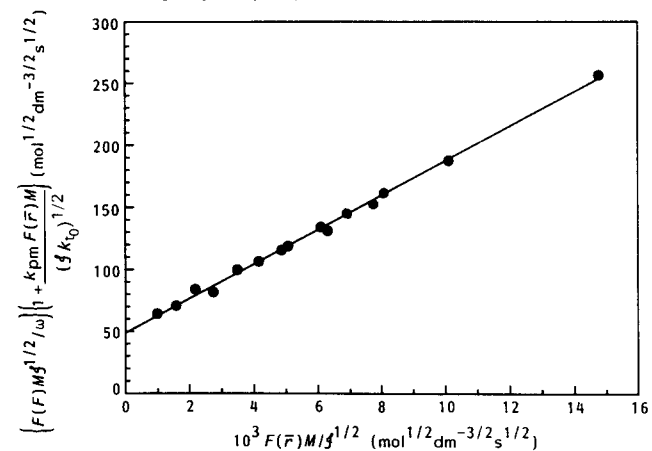


Figure 7 Plot of data in Table 1 according to equation (17) ( $F \equiv F(\bar{r})$ ) with parameters in Tables 1 and 2 (size-dependent  $k_i$ )

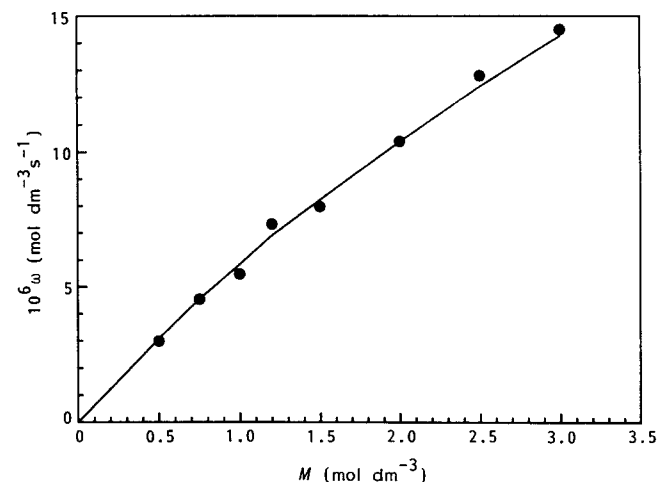


Figure 8  $\omega$ - $M$  relation with  $f = 1.814 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$  calculated from equation (16) ( $F \equiv F(\bar{r})$ ) with parameters in Tables 1 and 2 (size-dependent  $k_i$ ): experimental points

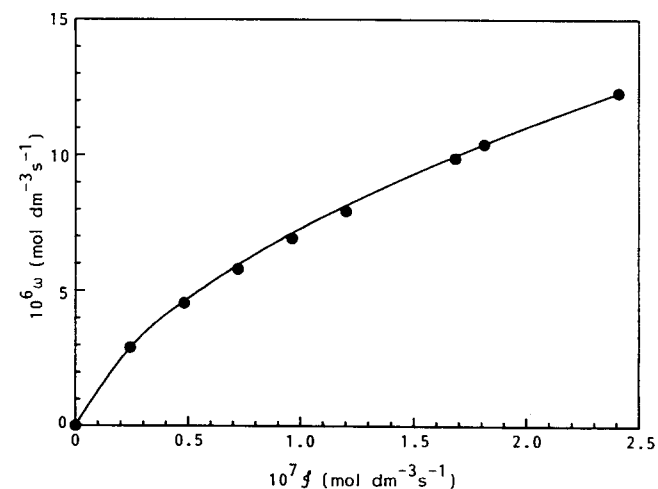
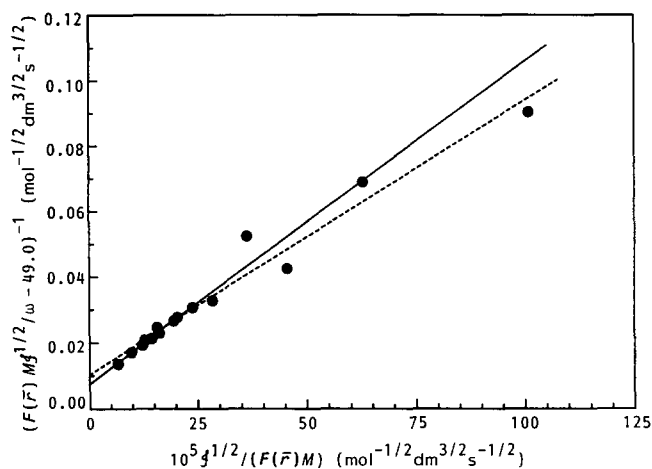


Figure 9  $\omega$ - $f$  relation with  $M = 2.0 \text{ mol dm}^{-3}$  calculated from equation (16) ( $F \equiv F(\bar{r})$ ) with parameters in Tables 1 and 2 (size-dependent  $k_i$ ): experimental points



**Figure 10** Plot according to equation (18) ( $F \equiv \bar{F}$ ) including all data points. Regression lines: full line – 10 points chosen as in Figures 2 and 6 (see text); broken line – 15 points

order for the three sets of  $F$  values. This order is not manifest in the data of Table 2, probably because corresponding  $F$  values in the three sets are not accurately proportional over the range.

The results described (Figures 3, 4, 8, 9) show that the data of Romani and Weale<sup>1</sup> can be fitted, probably within experimental error, by mechanisms based on degradative addition kinetics involving either constant or size-dependent  $k_t$ . The evaluated kinetic parameters are different in the two cases (Table 2), the main difference lying in the importance of re-initiation (equation 1e) which is virtually negligible when  $k_t$  is constant. It thus becomes of interest to see whether additional information on this process can be obtained. In principle there are three possibilities. First, the most favourable conditions for kinetic observation of  $k_{pm}$  are high monomer concentrations and low rates of initiation. (Thus, in Figures 2 and 6, evaluation of an intercept proportional to  $k_{pm}$  involves extrapolation of  $\mathcal{J}^{1/2}/M$  to zero.) In these circumstances, for

$$\frac{(\mathcal{J}k_{t_0})^{1/2}}{FM(k_{pm} + k_f)} \ll 1 \quad (23)$$

the rate of polymerization (equation 16) becomes

$$\omega = \mathcal{J}^{1/2} \frac{k_p}{k_{pm} + k_f} \left[ \frac{k_{pm} FM}{k_{t_0}^{1/2}} + \mathcal{J}^{1/2} \frac{k_f}{k_{pm} + k_f} + 0 \left\{ \frac{(\mathcal{J}k_{t_0})^{1/2}}{FM(k_{pm} + k_f)} \right\}^2 \right] \quad (24)$$

so that the  $\omega$ - $M$  plot tends to become linear, with slope:

$$k_p F \left( \frac{\mathcal{J}}{k_{t_0}} \right)^{1/2} \frac{k_{pm}}{k_{pm} + k_f} \quad (25)$$

and intercept (on  $\omega$  axis):

$$\frac{\mathcal{J}k_p k_f}{(k_{pm} + k_f)^2}$$

It is assumed in the above that  $F$  is sensibly constant under the conditions mentioned. This is likely to be a good approximation because high degrees of

polymerization and consequently large radical sizes will be favoured. According to equation (25), the slope is a measure of  $k_{pm}$ . For example, with the parameters (from  $F(\bar{r})$ ), in Table 2, the calculated slopes for  $\mathcal{J} = 1.814 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$  are  $2.6 \times 10^{-6} \text{ s}^{-1}$  and  $2.8 \times 10^{-7} \text{ s}^{-1}$  for size-dependent and constant  $k_t$ , respectively (taking  $F(\bar{r}) = 1.15$ , a little higher than the largest value in Table 1). The corresponding calculated intercepts are  $9.8 \times 10^{-6}$  and  $5.1 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ , respectively. Unfortunately the experimental conditions in equation (23) would be difficult to realize even if  $k_t$  is size dependent. With a maximum value of monomer concentration obtainable of about  $3 \text{ mol dm}^{-3}$  it would be necessary for  $\mathcal{J}^{1/2} \ll 8 \times 10^{-4}$  and  $\mathcal{J} \ll 6 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$ . Probably  $\mathcal{J} = 6 \times 10^{-9} \text{ mol dm}^{-3} \text{ s}^{-1}$  would be the highest acceptable rate of initiation which is approximately 25% of the lowest value in Table 1. Rates of polymerization would, therefore, be inconveniently, though not impossibly, low. However, to satisfy equation (23) for constant  $k_t$  much lower values of  $\mathcal{J}$  would be required (Table 2).

The second possibility is that observation of the polymerization under heterogeneous conditions with precipitated polymer could provide information on  $k_{pm}^2$ . It is possible under appropriate conditions for most of the radicals to react by degradative addition, with relatively little bimolecular termination. In this case, if  $k_{pm} = 0$ , radical occlusion (precipitation) will not produce a significant increase in rate of polymerization as commonly encountered in simple polymerizations. An appreciable enhancement of rate indicates a contribution from re-initiation. The experimental conditions required are  $\mathcal{J}^{1/2}/FM < k_f/k_{t_0}^{1/2}$  which as discussed above, is an inconvenient condition.

The third possibility is that since each re-initiation step equation (1e) leaves a residual vinyl double bond in a five-membered ring, re-initiation could be estimated, in principle, from the double bond content of the polymer. The fraction  $\phi$  of S· radicals formed which re-initiate is

$$\phi = \frac{k_{pm} FM}{k_{pm} FM + (\mathcal{J}k_{t_0})^{1/2}} \quad (26)$$

and the ratio of the number of degradative additions to normal propagation is  $k_f/k_p$ . Hence the ratio of double bonds to monomer units in the polymer is

$$\phi \frac{k_t}{k_p} = \frac{k_f}{k_p} \frac{k_{pm} FM}{k_{pm} FM + (\mathcal{J}k_{t_0})^{1/2}} \quad (27)$$

This quantity, like those discussed above, depends on  $\mathcal{J}^{1/2}/FM$ , but it is obviously less than  $k_f/k_p$ , or about 1% (Table 2). In the most favourable case in Table 1 ( $M = 2.00 \text{ mol dm}^{-3}$ ,  $\mathcal{J} = 0.241 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$ ) the content of double bonds estimated from equation (27) is 0.53% (calculated from  $F(\bar{r})$ ). Some of the double bonds remaining may be consumed by subsequent grafting or cross-linking reactions.

## ACKNOWLEDGEMENTS

We are pleased to thank Professor J. C. Bevington for drawing our attention to the paper of Romani and Weale.

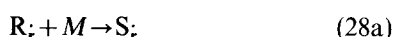
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## APPENDIX 1

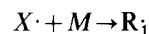
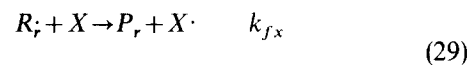
## Molecular weight distributions

Calculation of the distribution for constant  $k_t$  and effectively constant  $[M]$  and  $\mathcal{J}$  may be carried out by conventional methods with the aid of a small modification in equations (1d,e) so that these become



We estimate errors so introduced to be of the order 1%.

In the following  $P_r$  represents the concentration of polymer chains with  $r$  monomer units formed in time  $t$ . We have included non-degradative transfer to species  $X$ , with rate coefficient  $k_{fx}$  and transfer constant  $C_x$ :



To avoid heavy algebra it is convenient to express quantities in terms of the measurable  $\omega$ ,  $\mathcal{J}$  as far as possible. We then find:

$$R_i = \frac{\omega}{k_p M} (1 - \alpha) \alpha^{r-1} \quad (30)$$

$$S_i = \frac{k_f M}{k_{pm} M + (\mathcal{J} k_t)^{1/2}} R_i = \frac{k_f M}{k_{pm} M + (\mathcal{J} k_t)^{1/2}} R_i \alpha^{r-1} \quad r \geq 1$$

where

$$\alpha = \frac{k_{pm} M (k_p M + k_f M) + k_p M (\mathcal{J} k_t)^{1/2}}{\{k_p M + k_f M + k_{fx} X + (\mathcal{J} k_t)^{1/2}\} \{k_{pm} M + (\mathcal{J} k_t)^{1/2}\}} \quad (31)$$

Proceeding in the conventional fashion we have

$$\frac{dP_r}{dt} = \frac{k_t}{2} \sum_{s=1}^{r-1} R_{r-s} R_s + k_t \sum_{s=1}^{r-1} R_{r-s} S_s + \frac{k_t}{2} \sum S_{r-s} S_s + k_{fx} X R_r \quad (32)$$

which, with the aid of equation (30) and some manipulation, becomes

$$\frac{dP_r}{dt} = \frac{\mathcal{J}}{2} (r-1)(1-x)^2 \alpha^{r-2} + C_x \frac{X}{M} \omega (1-\alpha) \alpha^{r-1} \quad (33)$$

Hence, under stationary conditions, we obtain the required distribution

$$P_r = \frac{\mathcal{J} t}{2} (r-1)(1-x)^2 \alpha^{r-2} + \Delta M C_x \frac{X}{M} \omega (1-\alpha) \alpha^{r-1} \quad (34)$$

since  $\omega t = \Delta M$ , the total concentration of monomer polymerized.

To calculate the second and third moments of the distribution we note that with the 'long chain' approximation,  $k_p M \gg k_f M + k_{fx} X + (\mathcal{J} k_t)^{1/2}$ , so that equation (31) gives

$$1 - \alpha = \frac{\mathcal{J}}{\omega} + C_x \frac{X}{M} \quad (35)$$

The first three moments are presented in equation (36)

$$\sum_1^{\infty} P_r = \frac{\mathcal{J} t}{2} + \Delta M C_x \frac{X}{M}$$

$$\sum_1^{\infty} r P_r = \Delta M \quad (36)$$

$$\sum_1^{\infty} r^2 P_r = \frac{\Delta M \left( 3\mathcal{J} + 2C_x \frac{X}{M} \omega \right)}{\left( \mathcal{J} + C_x \frac{X}{M} \omega \right)^2}$$



Thus

$$\bar{P}_n = \frac{\sum_1^{\infty} rP_r}{\sum_1^{\infty} P_r} = \frac{\Delta M}{\frac{\mathcal{J}t}{2} + \Delta MC_x \frac{X}{M}} = \frac{\omega}{\frac{\mathcal{J}}{2} + C_x \frac{X}{M} \omega} \quad (37)$$

or

$$\frac{1}{\bar{P}_n} = \frac{\mathcal{J}}{2\omega} + C_x \frac{X}{M} \quad (38)$$

$$\bar{P}_w = \frac{\sum_1^{\infty} r^2 P_r}{\sum_1^{\infty} r P_r} = \frac{\omega \left( 3\mathcal{J} + 2C_x \frac{X}{M} \omega \right)}{\left( \mathcal{J} + C_x \frac{X}{M} \omega \right)^2} \quad (39)$$

Hence

$$\frac{\bar{P}_w}{\bar{P}_n} = \frac{\left( 3\mathcal{J} + 2C_x \frac{X}{M} \omega \right) \left( \mathcal{J} + 2C_x \frac{X}{M} \omega \right)}{2 \left( \mathcal{J} + C_x \frac{X}{M} \omega \right)^2} \quad (40)$$

so that the heterogeneity ratio has the values 1.5 and 2.0 for negligible and dominating transfer, respectively, as in conventional free-radical polymerization with termination by combination. Re-initiation does not play any distinguishable part in these calculations.

## APPENDIX 2

### Radical attack on acenaphthylene: molecular orbital calculations

The reactivity of acenaphthylene towards radicals was examined by semi-empirical MO theory using the AM1<sup>30</sup> method as implemented in the MOPAC program<sup>31,32</sup>. Radicals were treated as doublets in a restricted Hartree-Fock approach. Thus contamination by higher spin states was not permitted and comparisons amongst the molecules would be more meaningful. Methyl radical was chosen as a model for the attacking radicals.

Enthalpies of reaction for radical addition and hydrogen abstraction at sites 1 and 8 were calculated and are compared (Table A1) with attacks on ethylene. The

**Table A1** Heats of reaction (kcal mol<sup>-1</sup>), calculated, gas-phase conditions

CH <sub>3</sub> additions	
to ethylene	-37
to site 1	-43
to site 8	-27
H abstraction by CH <sub>3</sub>	
from ethylene	+6
from site 1	+22
from site 8	+15

radical additions are clearly favoured over hydrogen abstraction and CH<sub>3</sub> addition to site 1 is 16 kcal/mol more exothermic than addition to site 8. Thus the stability of the radical formed by addition at site 1 makes that the preferred site for attack if the process is under thermodynamic control.

If kinetic control is operative, one would ideally wish to look at activation energies for forming the activated complexes. This is exceedingly difficult, but a reasonable comparison of the reactivity at possible sites can be obtained from Fukui indices<sup>33</sup>. Here the Fukui index at an atom *a* acting as an electrophile being attacked by a nucleophile with a HOMO energy *E*<sub>ref</sub> is given by

$$F_{\text{El},a} = \sum_{i=\text{HOMO}+1} \sum_{j=\text{atom } a} \frac{n_i C_{j,i}^2}{E_i - E_{\text{ref}}}$$

where *n*<sub>*i*</sub> = 2 for closed shell systems, *C*<sub>*j,i*</sub> is the coefficient of AO *j* in the expansion of MO *i* and *E*<sub>*i*</sub> is the energy of orbital *i*. It is essentially a measure, MO by MO and weighted by the energy gap, of the amount of electron density that could be accepted at the given atomic centre. These indices are often dominated by the frontier orbitals, and for a molecule being attacked by a radical the LUMO density at each site may be a sufficient indicator of site preference<sup>34</sup>. Table A2 lists the indices for neutral acenaphthylene; they all indicate that there are many sites of comparable reactivity towards radical addition.

We also wanted to examine the ability of the product radicals to sustain chain growth (i.e. to act as nucleophiles in attacking acenaphthylene). Table A3 lists the Fukui nucleophilic indices (*F*<sub>*Nu*</sub>) and LUMO densities for these radicals.

Thus radical addition at site 1 produces a radical that could be expected to sustain chain propagation much more effectively than would the radical formed by addition at site 8.

**Table A2** Reactivity indices

Site	1	5a	6	7	8	8a	8b
Neutral parent							
<i>F</i> <sub>El</sub>	0.66	0.64	0.70	0.64	0.70	0.66	0.63
<i>F</i> <sub>El(LUMO)</sub> <sup>a</sup>	0.11	0.00	0.15	0.04	0.12	0.11	0.00
LUMO density	0.22	0.00	0.28	0.06	0.24	0.20	0.00

<sup>a</sup>LUMO contribution

**Table A3** Reactivity indices for radicals

Site	2	3	8a
CH <sub>3</sub> added at site 1			
<i>F</i> <sub><i>Nu</i></sub> <sup>a</sup>	0.43		
LUMO density	0.82	0.08	
CH <sub>3</sub> added at site 8			
<i>F</i> <sub><i>Nu</i></sub>	0.09		0.27
LUMO density	0.19	0.06	0.60

<sup>a</sup>Here the summation is over the occupied orbitals; occupancy is 1.0 for the half-filled orbital and the reference energy is the LUMO of acenaphthylene