

## The reactivities towards the benzoyloxy radical of various isomers of fluorostilbene

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### Summary

The rate constants at 60°C for the reactions of the benzoyloxy radical with methyl methacrylate, the E-isomers of 2-, 3- and 4-fluorostilbene and the Z-isomer of 4-fluorostilbene have relative values of 1, 41, 17, 18 and 14 respectively. These results were obtained from work involving analyses for the benzoate and phenyl end-groups in polymers of methyl methacrylate, prepared using benzoyl peroxide suitably labelled with carbon-14 and tritium using each of the fluorostilbenes in turn as an additive in a polymerization.

### Introduction

Several papers (1) have referred to the high reactivities of the E-isomers of stilbene (STL) and related substances, such as the distyrylbenzenes and 1,4-diarylbuta-1,3-dienes, towards the benzoyloxy radicals formed by the thermal dissociation of benzoyl peroxide (BPO). High reactivity for the radical is also shown by the E-isomers of derivatives of STL having substituents (such as phenyl, -OH, -OMe and -Cl) at the 4-positions. A point of interest arising from these studies is the possibility of preparing polymers containing end-groups of new types, represented as Ph·CO·O·A- where A stands for a unit derived from a STL-like substance by opening of the central C=C double bond. It is necessary only to polymerize a monomer with BPO as initiator in the presence of the STL-like substance at quite low concentration.

The work has been extended to examination of the E-isomers of 2-, 3- and 4-fluorostilbene (2-FS, 3-FS and 4-FS respectively) and also the Z-isomer of the 4-substituted compound (z4-FS). Their reactivities towards the benzoyloxy radical were assessed by a method (2) involving the use of BPO labelled with carbon-14 at the carbonyl sites and with tritium in the rings (\*BPO). The doubly labelled peroxide was used to initiate polymerizations at 60°C of methyl methacrylate (MMA) containing a ring-fluorinated STL at a low concentration. The <sup>14</sup>C and <sup>3</sup>H activities of the polymers were then compared with those of the sample of \*BPO used in their preparations. A well tested procedure was then applied to compare the rate constants for the additions of the benzoyloxy radical to MMA and to the various derivatives of STL, using the decarboxylation of the radical as a reference reaction. Monomers other than MMA can be used in work of this type but MMA is particularly convenient because it has comparatively low reactivity towards the radical and its polymerization is well characterized.

### Experimental

The fluorostilbenes were prepared by phase-transfer catalyzed Wittig reactions (3). For 2- and 3-FS, the starting materials were benzyltriphenyl phosphonium chloride and the appropriate fluorobenzaldehyde. After recrystallization from methanol, the products had melting points agreeing with the

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published values (4,5) and were found by TLC and capillary GC/MS to be homogeneous. 4-FS and z4-FS were prepared from 4-fluorobenzyltriphenylphosphonium chloride and benzaldehyde. 4-FS was recrystallized from methanol and its purity was confirmed as in the cases of 2- and 3-FS. z4-FS was recovered from the liquor and purified by flash chromatography and distillation under reduced pressure, to give a clear oil, shown to be homogeneous by TLC and capillary GC/MS. Other materials were prepared and/or purified as described previously (2).

Polymerizations were conducted at 60°C under anaerobic conditions using MMA at  $3 \cdot 10 \text{ mol dm}^{-3}$  in toluene; conversions were below 10%. Polymers were recovered by precipitation in methanol; they were purified by three precipitations. Radioactive assays were performed by scintillation counting of solutions.

### Results and Discussion

Dilatometric measurements showed that the fluorostilbenes had almost no effect on the rate of polymerization ( $R_p$ ) of MMA at 60°C with BPO, at least when the additives were used at concentrations up to about  $12 \times 10^{-2}$  molar. Previous work with 14C-labelled 4-FS as a comonomer with MMA, using azobisisobutyronitrile as initiator, showed that its incorporation is slight (6). Taking MMA as monomer-1, the reactivity ratios  $r_1$  and  $r_2$  are over 200 and close to zero respectively; if  $[MMA]/[4-FS]$  in the feed is 40, a value generally similar to those used in the present work, the growth steps lead to the incorporation of more than 8000 MMA units for each 4-FS unit. The polymerization in the presence of 4-FS can therefore be regarded as effectively the homopolymerization of MMA and the product as a homopolymer. There are clear indications (7) that the same considerations apply to systems involving the other fluorostilbenes.

Table 1 refers to polymerizations initiated by \*BPO. The 3H-activity of a polymer provides a measure of the total content of initiator fragments in the polymer, corresponding to both benzoate and phenyl end-groups; the activity is therefore inversely proportional to the average kinetic chain length during the polymerization so that it is proportional to (rate of initiation)/ $R_p$ . For a set of polymers obtained from reactions for which (a)  $[MMA]$  is fixed although  $[*BPO]$  is varied, (b)  $R_p$  is proportional to  $[*BPO]^{1/2}$  and (c) the rate of initiation is directly proportional to  $[*BPO]$ , (3H-activity of polymer)/ $[*BPO]^{1/2}$  should have a constant value; the results in the Table lead to values of this quantity between 7200 and 7730  $\text{Bq g}^{-1} \text{ mol}^{-1/2} \text{ dm}^{3/2}$ . The

TABLE POLYMERIZATIONS OF METHYL METHACRYLATE INITIATED BY DOUBLY LABELLED BENZOYL PEROXIDE

Expt. no.	$10^2[\text{additive}]$ in $\text{mol dm}^{-3}$	$10^2[*BPO]$ in $\text{mol dm}^{-3}$	$10^{-2}(\text{activity of polymer in Bq g}^{-1})$	
			carbon-14	tritium
1	4-FS; 4.48	0.45	0.85	4.93
2	4-FS; 6.78	1.05	1.41	7.65
3	z4-FS; 9.60	1.21	1.39	8.40
4	3-FS; 5.46	0.41	0.79	4.95
5	2-FS; 12.84	0.54	0.95	5.32
6	-	0.92	0.95	6.90

$$[\text{methyl methacrylate}] = 3 \cdot 10 \text{ mol dm}^{-3}$$

activities ( $\text{Bq g}^{-1}$ ) of \*BPO: carbon-14,  $2.87 \times 10^5$ ; tritium,  $10.04 \times 10^5$ .

narrowness of the range of values suggests that there are no kinetic abnormalities for the polymerizations.

A fraction  $\underline{x}$  for a polymer is defined as (no. of benzoate end-groups)/(sum of nos. of benzoate and phenyl end-groups) so that  $\underline{x}/(1-\underline{x})$  is (no. of benzoate end-groups)/(no. of phenyl end-groups). Values of  $\underline{x}$  can be found by means of the relationship

$$\underline{x} = \frac{3\text{H-activity of peroxide}}{14\text{C-activity of peroxide}} \times \frac{14\text{C-activity of polymer}}{3\text{H-activity of polymer}}$$

Rate constants  $k_1$ ,  $k_2$  and  $k_2'$  refer respectively to the decarboxylation of the benzoyloxy radical, the addition of that radical to MMA and its attachment to the additive. The equation

$$\frac{\underline{x}}{1-\underline{x}} = \frac{k_2[\text{MMA}]}{k_1} + \frac{k_2'[\text{additive}]}{k_1}$$

has been derived (2) and found to be generally applicable for determination of  $k_2/k_1$ ,  $k_2'/k_1$  and  $k_2'/k_2$ .

The activities of polymer-6 lead to  $k_2/k_1 = 0.30 \text{ mol}^{-1} \text{ dm}^3$ , in satisfactory agreement with the accepted value of  $0.31 \text{ mol}^{-1} \text{ dm}^3$ . The results for polymers-1-5 give values of  $k_2'/k_1$  in  $\text{mol}^{-1} \text{ dm}^3$  as 12.7, 12.7, 4.3, 5.7 and 5.4 respectively. The coincidence of the two values for 4-FS can be noted.

The relative reactivities towards the benzoyloxy radical, given by  $k_2'/k_2$ , of 4-FS, z4-FS, 3-FS and 2-FS can be taken as 41, 14, 18 and 17 respectively in terms of the reactivity of MMA being unity; for STL itself, the value is ~40. The results are of course subject to some uncertainty and they are very sensitive to small changes in the fraction  $\underline{x}$ ; changes of  $\pm 3\%$  in that quantity for the polymers prepared using 4-FS, for example, lead to extreme values of 32 and 48 and for the polymer made using 2-FS to extremes of 11 and 21. Even allowing for these wide ranges, it is clear that z4-FS, 2-FS and 3-FS are considerably less reactive than 4-FS.

The factor of about three between the reactivities of 4-FS and z4-FS matches those found for the E- and Z-isomers of other STL-like compounds in their reactions with the benzoyloxy radical; a good illustration is provided by the E,E-, E,Z- and Z,Z-isomers of 1,4-distyrylbenzene (8,9) for which the reactivities towards the radical are in the proportions 4.3: 1.6: 1. Walling (10) discussed differences between the reactivities towards carbon-centred radicals for the E- and Z-isomers of various unsaturated compounds including STL.

The introduction of a fluorine atom at the 4-position in the molecule of STL has little effect on the reactivity towards the benzoyloxy radical. It seems likely therefore that the appreciable reduction in reactivity caused by the presence of fluorine at the 2- or 3-position is not connected with steric effects or with effects of the substituent upon the stability of the adduct radical; these factors have recently been discussed (11) for reaction of the 2-cyano-2-propyl radical with alkenes. It is possible that the lower reactivities of 2-FS and 3-FS are associated with deviations from planarity of the molecules.

The experiments now reported give no information about which site in a molecule of a fluorostilbene corresponds to the point of attachment of a benzoyloxy radical; in particular, it is not possible to distinguish between a benzoate group attached to the carbon atom also carrying a phenyl group and one joined to the carbon atom bearing a fluorophenyl group. In principle, questions about regioselectivity in such cases can be answered by application of NMR methods; examples of this approach can be cited for addition of the benzoyloxy radical to styrene or to 4-FS. Australian workers (12) first showed that, in polystyrene prepared using BPO enriched with carbon-13, an appreciable proportion of the benzoate end-groups are attached to the heads (i.e. -CHPh- groups) of styrene units rather than to the tails; some of these

structures result from the direct reaction of benzoyloxy radicals with the heads of monomer molecules. An examination (13) by fluorine-19 NMR of the 4-FS units adjacent to benzoate end-groups in polystyrene, prepared using BPO as initiator with 4-FS as an additive, led to the conclusion that there are approximately equal chances for the benzoyloxy radical to add at either end of the central C=C bond in the molecule of 4-FS. It is probably relevant to note that head-to-head growth reactions seem to be much more likely to occur during the radical polymerizations of fluorine-containing monomers, such as vinyl fluoride and vinylidene fluoride, than during the polymerizations of other monomers (14).

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