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Comparison of some 4- and 4,4′-substituted derivatives of stilbene for their reactivities towards the benzoyloxy radical

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Summary

4-Fluoro- and 4,4'-difluorostilbene are similar in their reactivities towards the benzoyloxy radical; a similar conclusion has been reached in respect of 4-chloro- with 4,4'-dichlorostilbene and 4-phenyl- with 4,4'-diphenylstilbene. These results have been obtained by consideration of the numbers of benzoate and phenyl end-groups in poly(methyl methacrylate) made using benzoyl peroxide in the presence of the appropriate derivative of stilbene.

Introduction

Stilbene (STL) and many of its derivatives and analogues are very effective in capturing the benzoyloxy radical; high reactivity towards the radical is possessed also by certain other substances, e.g. 1,4-diphenylbuta-1,3-diene, having molecules with aryl groups and extensive conjugation (1). The high reactivity of STL is evident on considering the rate constants for the reactions at 60°C of the benzoyloxy radical with methyl methacrylate (MMA), styrene (STY) and the E-isomer of STL; their relative values are 1, 8 and 48 respectively.

A polymer, made using benzoyl peroxide (BPO) as initiator with a STL-like substance as an additive, is expected to have benzoate and phenyl end-groups in relative numbers rather different from those for the corresponding polymer made in the absence of the additive. The presence of the additive in the polymerizing system is expected to cause the balance between the two types of incorporated initiator fragments to shift in favour of the ester end-groups many of which would be attached to units derived from the additive; the total incorporation in polymer of the STL-like substance is usually only slight.

The change in the relative numbers of benzoate and phenyl end-groups, caused by the presence of an additive during polymerization, forms the basis of a method for comparison of the reactivities of STL etc. towards the benzoyloxy radical using the decarboxylation of the radical (rate constant = k') as a reference reaction. One procedure requires BPO labelled in the rings with tritium and in the carbonyl groups with carbon-14; it is used as initiator for polymerization of MMA containing the substance under examination, at comparatively low concentration. From the specific activities of the polymer and the original peroxide, a quantity "x" defined as (no. of benzoate end-groups)/(sum of nos. of benzoate and phenyl end-groups) is found from the expression

$$x = \frac{\text{14C-activity of polymer}}{\text{3H-activity of polymer}} \times \frac{\text{3H-activity of peroxide}}{\text{14C-activity of peroxide}} \qquad \text{(i)}$$

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where the activities are expressed in units such as Bq/g. Use is then made of equation (ii)

$$\frac{x}{1-x} = \frac{k'''[\mathrm{MMA}]}{k'} + \frac{k''[\text{additive}]}{k'} \qquad \text{(ii)}$$

in which k'' and k''' are the rate constants for additions of the benzoyloxy radical to the additive and MMA respectively. A reliable value of k'''/k' is known (1) and so it is possible to find k''/k' and k''/k'''. There have been direct estimates of k', for example by Ingold and co-workers (2), and so absolute values of the various rate constants k'' can be deduced if required.

Studies have been made of the effects on reactivity towards the benzoyloxy radical of substituents, including fluorine, at the 4-position in one of the phenyl groups of STL (1); results have been quoted also for 4,4'-difluorostilbene (3). A report is now given of a comparison of the reactivities of 4-phenyl-, 4,4'-diphenyl-, 4-chloro- and 4,4'-dichlorostilbene as well as the 4-fluoro- and 4,4'-difluoro-derivatives. The results extend the information available on the reactivities of STL-like substances towards the benzoyloxy radical; they may help in the eventual understanding of the factors responsible for the high reactivities of those substances. There has been previous work on the reactions of the 4-chloro-, 4,4'-dichloro- (4) and 4-phenyl-derivatives of STL with the benzoyloxy radical (5). A procedure was applied involving BPO highly enriched with carbon-13 at the carbonyl sites, use of which was first reported by Solomon and co-workers (6) in connection with a detailed mechanistic study of the initiation by BPO of the polymerization of STY. The 13C-NMR spectrum was recorded for each polymer made using 13C-BPO in the presence of the STL-like substance. Integration of a spectrum made it possible to compare the number of benzoate end-groups attached to units derived from the additive with the number adjacent to units derived from the principal monomer. The equation

$$\frac{\text{no. of Ph}\cdot\text{CO}\cdot\text{O}\cdot\text{(additive)- end-groups}}{\text{no. of Ph}\cdot\text{CO}\cdot\text{O}\cdot\text{(monomer)- end-groups}} = \frac{k''[\text{additive}]}{k'''[\text{monomer}]} \qquad \text{(iii)}$$

was then applied for assessment of the reactivity of the additive.

Experimental

4,4'-Diphenylstilbene (Lancaster Synthesis) was described as "99%; for scintillation work"; it was used as received. The other derivatives of STL (the E-isomer in each case) were prepared by phase-transfer catalyzed Wittig reactions (7) and purified and characterized by routine procedures. Other materials were prepared and/or purified as described already (8). Polymerizations were performed at 60°C anaerobically; they were monitored by dilatometry and conversions did not exceed 10%. Polymers were recovered and purified by four precipitations in methanol; it has been confirmed that the treatment is amply sufficient for virtually complete removal of undecomposed BPO from polyMMA (9). Polymers were finally dried in vacuum. Scintillation counting of solutions was used for assay of radioactive materials.

Results and Discussion

The STL derivatives, at the concentrations considered here, had little if any effect on the rate of polymerization of MMA initiated by BPO at 60°C. Data on polymerizations and the derived polymers are presented in Table 1. The information for 4-fluorostilbene has been given elsewhere (10) but is repeated for ease of comparison. Table 1 shows values of "x" as defined in connection with equation (i) and calculated by means of that equation.

Application of equation (ii), using the values of "x", [MMA] and [additive] given in Table 1 and taking k'''/k' as 0·31 dm^3/mol, leads to values of k''/k''' (see Table 2) i.e. reactivities of the STL-derivatives towards the benzoyloxy radical taking that of MMA as unity; as stated already, the reactivity of the parent substance, STL, is 48 on the same scale. It should be noted that the Summary of the original publication (10) contains an error and the correct relative reactivity of 4-fluorostilbene is as given in the text of that paper.

Table 1. Polymerizations of MMA using 14C,3H-BPO and derivatives of STL

Expt. no.	concns. in mol/dm^3			10^{-2}(polymer activity (Bq/g))		
	10^2[BPO]	10^2[additive]	[MMA]	carbon-14	tritium	"x"
1	1·07 a	6·78 F	3·10	1·41	7·65	0·646
2	0·51 a	4·48 F	3·10	0·85	4·93	0·604
3	0·73 a	7·32 DF	3·10	1·25	6·43	0·681
4	0·56 a	4·48 DF	3·10	1·04	5·78	0·631
5	0·16 b	3·88 C	2·62	0·31	1·72	0·586
6	0·16 b	3·27 DC	2·62	0·29	1·70	0·563
7	0·49 b	1·07 P	2·86	0·40	2·41	0·544
8	0·40 b	0·55 DP	2·86	0·36	2·30	0·507

10^{-5}(BPO activity (Bq/g)):- carbon-14, 2·87; tritium (a) 10·04, (b) 9·33.
derivatives of STL :- F, 4-fluoro; DF, 4,4'-difluoro; C, 4-chloro;
DC, 4,4'-dichloro; P, 4-phenyl; DP, 4,4'-diphenyl.

Table 2. Reactivities of STL-derivatives towards the benzoyloxy radical

polymer no.	derivative of STL	relative reactivity	range
1	4-fluoro	41	34-49
2	4-fluoro	41	33-49
3	4,4'-difluoro	52	44-60
4	4,4'-difluoro	54	45-64
5	4-chloro	50	42-59
6	4,4'-dichloro	47	39-56
7	4-phenyl	92	69-116
8	4,4'-diphenyl	83	48-120

The derived values of k"/k' and k"/k"' are rather sensitive to quite small changes in "x". Table 2 includes a column headed "range", showing lower and upper limits for k"/k"' assuming uncertainties of up to ±3 % in "x". The range for 4,4'-diphenylstilbene is the widest because the low solubility of that substance meant that only a small concentration could be used;consequently, the value of "x" for polymer-8 was not very different from that for polyMMA made with the same concentration of monomer but in the absence of additive. It is encouraging that there is good agreement between results for the pairs of polymers nos. 1 & 2 and nos. 3 & 4.

Previous work (4,5) on the reactions of the 4-chloro-, 4,4'-dichloro- and 4-phenyl-derivatives of STL with benzoyloxy radical, depending on the use of 13C-BPO, gave relative reactivities of 90, 37 and 104 respectively. There is similarity between the older results and those now given for the 4,4'-dichloro- and 4-phenyl- compounds but a great discrepancy exists between the two values for 4-chlorostilbene. It should be noted that, in the previous study, the NMR spectrometer was being used close to the limit of its sensitivity so that integration of the spectrum was inevitably somewhat uncertain suggesting that the present result should be preferred.

It is concluded that introduction of fluorine or chlorine at the 4-position in STL has little effect on the reactivity towards the benzoyloxy radical but that quite a large increase is caused by the placing of a phenyl group at that site. For all three substituents, little or no change is produced by a second substitution at the 4'-position. Close similarity between STL and its 4-fluoro- and 4,4'-difluoro-derivatives was found also for their reactivities towards the polySTY radical, as deduced from studies of copolymerizations (3).

References

1. J.C.Bevington, Angew. Makromol. Chem. 185/186, 1 (1991).
2. J.Chateauneuf, J.Lusztyk and K.U.Ingold, J. Am. Chem. 110, 2886 (1988).
3. J.C.Bevington, S.W.Breuer, T.N.Huckerby and R.Jones, Polym. Bull. 34, 37 (1995).
4. J.C.Bevington, S.W.Breuer and T.N.Huckerby, Angew. Makromol. Chem. 140, 145 (1986).
5. J.C.Bevington, S.W.Breuer and T.N.Huckerby, Macromolecules 22, 55 (1989).
6. G.Moad, D.H.Solomon, S.R.Johns and R.I.Willing, Macromolecules 15, 1188 (1982).
7. G.Märkl and A.Merz, Synthesis 295 (1973).
8. J.C.Bevington, S.W.Breuer and T.N.Huckerby, Polym. Bull. 12, 531 (1984).
9. C.A.Barson, J.C.Bevington and B.J.Hunt, Eur. Polym. J. in the press.
10. C.A.Barson, J.C.Bevington and S.W.Breuer, Polym. Bull 32, 625 (1994).