

# Incorporation of stilbene and *p*-fluorostilbene in polystyrene during radical polymerization

J. C. Bevington, T. N. Huckerby and N. Vickerstaff

Department of Chemistry, The University, Lancaster, LA1 4YA, UK

and C. A. Barson

Department of Chemistry, The University, Birmingham, B15 2TT, UK

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Samples of *trans*-stilbene and *trans-p*-fluorostilbene labelled with  $^{14}\text{C}$  have been used for measurement of the small extents to which they copolymerize with styrene during radical polymerization. Copolymers of styrene with *p*-fluorostilbene have been examined by  $^{19}\text{F}$  n.m.r.; there are important differences between the spectra for products made using benzoyl peroxide and azobisisobutyronitrile as initiators. The results are explained in terms of a high probability of a stilbene unit being adjacent to the ester end-group derived from an aryloxy radical.

(Keywords: radical polymerization; styrene; stilbene; perfluorostilbene,  $^{19}\text{F}$  nuclear magnetic resonance; carbon-14)

## INTRODUCTION

Stilbene (STL) is rather unreactive as a comonomer with styrene (STY) in radical polymerization and shows low reactivity towards the polystyrene radical<sup>1</sup> but it is very reactive towards the benzoyloxy radical<sup>2</sup>. When benzoyl peroxide (BPO) enriched in its carbonyl groups with  $^{13}\text{C}$  is used to initiate the polymerization of STY, the resulting benzoate end-groups can be detected by  $^{13}\text{C}$  n.m.r. spectroscopy. Additional end-group signals are readily detected for polymers produced in systems also containing STL at quite low concentrations; these signals arise from benzoate groups attached to STL units and it is possible to compare the number of such groups with the number of the ester end-groups attached to STY units<sup>3</sup>. The comparatively few STL units in copolymers of STY with STL, prepared with BPO as initiator, are not distributed uniformly through the macromolecules and there is an excess at sites adjacent to benzoate end-groups. Very similar effects arise when *p*-fluorobenzoyl peroxide (FBPO) is used as initiator instead of BPO<sup>4</sup> but there is no evidence for an excess of STL units adjacent to 2-cyano-2-propyl end-groups derived from azobisisobutyronitrile (AIBN)<sup>3</sup>.

During work involving STY with FBPO and *trans-p*-fluorostilbene (FSTL), it became necessary to have information on the total incorporation in polySTY of FSTL, i.e. at in-chain sites as well as at those adjacent to chain-ends. For this purpose,  $^{14}\text{C}$ -FSTL was used so that high sensitivity could be achieved in the analyses. The opportunity was taken to perform experiments also with  $^{14}\text{C}$ -STL using either FBPO or AIBN as initiator. The results of these tracer experiments are now presented and compared with those of Cameron and Grassie<sup>1</sup>, who used  $^3\text{H}$ -STL in similar studies. There is also an account of an examination by  $^{19}\text{F}$  n.m.r. of copolymers of STY with FSTL, leading to information on the positions of the FSTL units in the macromolecules.

## EXPERIMENTAL

Monomers, initiators and solvents were purified by standard procedures. The  $^{14}\text{C}$ -labelled stilbenes were prepared by phase transfer catalysed Wittig reactions<sup>5</sup> involving  $^{14}\text{C}$ -carbonyl-benzaldehyde (Amersham International) with either benzyltriphenylphosphonium chloride or *p*-fluorobenzyltriphenylphosphonium chloride; the specific activities of the products were approx. 14.9  $\mu\text{Ci/g}$  (STL) and 13.5  $\mu\text{Ci/g}$  (FSTL), i.e. 551 and 500 kBq/g respectively.

Polymers were prepared at 60°C under air-free conditions with benzene as diluent; the concentrations of STY were close to 4 mol l<sup>-1</sup> and conversions did not exceed 8%. Polymers were recovered by precipitation in methanol and purified by three reprecipitations. Number-average molecular weights were measured by g.p.c. using equipment supplied by Waters Associates and calibrated for polystyrene.

The specific activities of  $^{14}\text{C}$ -materials were determined using an LKB-Wallac 'Spectral' 1219 Liquid Scintillation Counter. Weighed samples were dissolved in a toluene-butyl PBD liquid scintillation mixture. Corrections for quenching were made using the spectral quench parameter method with an external standard. This method uses the calibrated shift of the external standard spectrum as a means of determining the efficiency of counting for each sample.

$^{19}\text{F}$  n.m.r. spectra were recorded at 93.7 MHz using a JEOL FX100 spectrometer with a 5 mm probe, operating at ambient temperature. Samples of polymers (40–80 mg) were dissolved in  $\text{CDCl}_3$  (0.5 ml) containing a trace of fluorobenzene as internal reference (0.0 $\delta$ ) and filtered before use. Spectra 2000 Hz in width were accumulated into 4K (4096) data points and zero-filled to 16K data points before Fourier-transformation, introducing 1–1.5 Hz line-broadening in order to reduce baseline noise. The pulse repetition period was 3 s using a tip angle of 90°.

## RESULTS AND DISCUSSION

Table 1 gives information about the polymerizations and the resulting polymers. Tests on the removal from unlabelled polymers of added  $^{14}\text{C}$ -STL or  $^{14}\text{C}$ -FSTL showed that reprecipitation was effective for purification of polymers. At least 98.5% of the radioactivity found in the purified polymers 1–6 was due to chemically incorporated  $^{14}\text{C}$ -STL or  $^{14}\text{C}$ -FSTL and the activity associated with occluded material can be neglected.

For the polymers referred to in Table 1, the end-groups derived from the initiators contribute less than 1% to the total weights so that polymers 1–4 can be represented as  $(\text{C}_8\text{H}_8)_x(\text{C}_{14}\text{H}_{12})_y$  and polymers 5 and 6 as  $(\text{C}_8\text{H}_8)_x(\text{C}_{14}\text{H}_{11}\text{F})_z$  in calculations of the relative numbers of the monomeric units. The counting rates for polymer,  $^{14}\text{C}$ -STL and  $^{14}\text{C}$ -FSTL are taken as  $C_p$ ,  $C_s$  and  $C_f$  respectively, so that

$$\frac{C_p}{C_s} = \frac{180y}{104x + 180y} \quad \text{and} \quad \frac{y}{x} = \frac{104C_p}{180(C_s - C_p)} \quad \text{for polymers 1–4}$$

$$\frac{C_p}{C_f} = \frac{198z}{104x + 198z} \quad \text{and} \quad \frac{z}{x} = \frac{104C_p}{198(C_f - C_p)} \quad \text{for polymers 5 and 6.}$$

The values of  $10^2 y/x$  for polymers 1–4 and of  $10^2 z/x$  for polymer 5 and 6 are 0.41, 1.77, 0.30, 1.43, 0.60 and 1.33 respectively. These results refer to total contents of STL or FSTL in the polymers because the method of analysis cannot distinguish between units adjacent to end-groups as a result of an initiation process and units situated more centrally in the macromolecules as a result of growth reactions.

Studies by  $^{13}\text{C}$  n.m.r. have indicated that units corresponding to STL or its derivatives are not concentrated near 2-cyano-2-propyl end-groups<sup>3,6</sup>. This conclusion has been confirmed by examination by  $^{19}\text{F}$  n.m.r. of a STY/FSTL copolymer (polymer 7) prepared with BPO as initiator and a similar copolymer made using AIBN (polymer 8). Spectra A and B in Figure 1 very closely resemble one another in the spectral region –3.8 to –5.5 ppm; however, polymer 7 gives rise to additional signals between –0.8 and –1.8 ppm and around –3.5 ppm. To assist in the assignment of these signals, the compounds  $p\text{-F.C}_6\text{H}_4.\text{CH}_2.\text{CH}_2.\text{C}_6\text{H}_5$  and  $\text{C}_6\text{H}_5.\text{CO.O.CH}(\text{C}_6\text{H}_4.p\text{-F}).\text{CH}_2.\text{C}_6\text{H}_5$  were examined. The former resembles an in-chain FSTL unit and gives a  $^{19}\text{F}$  n.m.r. peak at –4.57 ppm. The ester resembles an FSTL unit adjacent to an initiator fragment and it gives a

signal at –2.03 ppm. It is concluded that, in the spectra of polymers 7 and 8, the signals between –3.8 and –5.5 ppm correspond to in-chain FSTL units which are present when either initiator is used; the two sets of additional signals for polymer 7 are associated with FSTL units adjacent to benzoate end-groups. The absence from the spectrum of polymer 8 of signals other than those between about –3.6 and –5.5 ppm confirms that there is negligible direct addition of the 2-cyano-2-propyl radical to FSTL. It is considered that the signals around –1 ppm arise from the structure produced by the attachment of the benzoyloxy radical to the carbon atom also carrying the *p*-fluorophenyl group (F-addition) and that the signals around –3.5 ppm correspond to attack at the other end of the carbon–carbon double bond in FSTL (H-addition). For all three groups of signals arising from FSTL units in the polymers, the complexity must be associated with stereochemical relationships with neighbouring STY units.

Spectrum C in Figure 1 is a difference-spectrum constructed from spectra A and B; it shows the

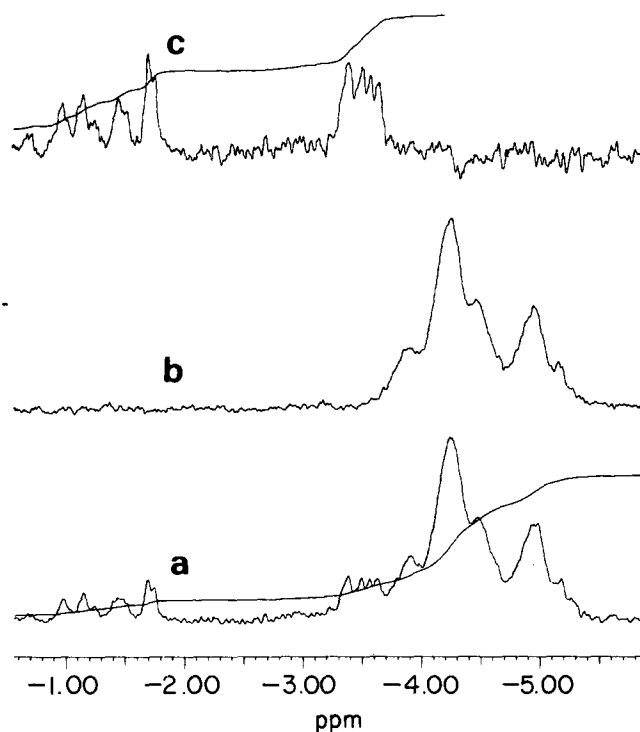


Figure 1  $^{19}\text{F}$  n.m.r. spectra of polymers. (A) Polymer 7, prepared from system in which  $[\text{STY}]/[\text{FSTL}] = 6.17$  with BPO as initiator. (B) Polymer 8, prepared from system in which  $[\text{STY}]/[\text{FSTL}] = 7.10$  with AIBN as initiator. (C) Difference-spectrum constructed from spectra A and B

Table 1 Polymerizations of styrene containing  $^{14}\text{C}$ -stilbene or  $^{14}\text{C}$ -fluorostilbene

Polymer no.	Type of stilbene <sup>a</sup>	$10^2 \cdot [\text{STL}]/[\text{STY}]^b$	$10^{-3} \times \bar{M}_n$	$10^{-5}$ (disintegrations/min/g) <sup>c</sup>
1	H	4.24	29.3	3.91
2	H	19.42	26.6	16.53
3 <sup>d</sup>	H	3.43	18.0	2.90
4 <sup>d</sup>	H	17.39	17.1	13.37
5	F	4.06	27.1	5.35
6	F	16.10	36.7	11.63

<sup>a</sup>H = *trans*-stilbene; F = *trans-p*-fluorostilbene

<sup>b</sup>STL refers to  $^{14}\text{C}$ -stilbene or  $^{14}\text{C}$ -*p*-fluorostilbene as appropriate and STY to styrene in polymerizing system

<sup>c</sup>Counting rates for purified polymers; corresponding values for  $^{14}\text{C}$ -STL and  $^{14}\text{C}$ -FSTL are 557.1 and 470.7 respectively

<sup>d</sup>AIBN used as initiator; FBPO used in the other cases

resonances associated with fluorine atoms in FSTL units attached directly to benzoate end-groups. From the areas under the two sets of peaks, it is deduced that the ratio of the number of F-additions to that of H-additions is 1:0.9. This information can be used, in conjunction with knowledge of the areas under peaks in spectrum A, to compare the numbers of FSTL units at in-chain and at end-of-chain sites. For spectrum A, let  $X$  be the area under the set of peaks at about  $-1.5$  ppm and  $Y$  be the total area under the peaks between  $-3.25$  and  $-5.50$  ppm;  $Y$  includes a contribution of  $0.9X$  from the set of peaks at about  $-3.5$  ppm. Then

$$\frac{\text{no. of in-chain FSTL units}}{\text{no. of end chain FSTL units}} = S = \frac{Y - 0.9X}{1.9X}$$

The value of  $Y/X$  is 9.25 so that  $S$  is 4.4.

Consider again the results of the experiments involving  $^{14}\text{C}$ -STL. It appears that the values of  $y/x$  for polymers 3 and 4, both prepared with AIBN as initiator, refer to in-chain STL units although of course there may be a few of these units situated very close to initiator fragments. The analytical results for these polymers can therefore be used legitimately for characterizing the growth reactions in the copolymerization of STY ( $M_1$ ) with STL. Accepting the argument of Cameron and Grassie<sup>1</sup>, the monomer reactivity ratio  $r_2$  is taken as close to zero; thus, for systems in which  $[M_2]$  is appreciably less than  $[M_1]$ , the instantaneous copolymer composition equation can be simplified to

$$\left(\frac{M_1}{M_2}\right)_{\text{copolymer}} = \frac{r_1[M_1]}{[M_2]} + 1$$

The derived values of  $r_1$  are 11 (polymer 3) and 12 (polymer 4) in good agreement with the value of  $11.2 \pm 1.2$  given by Cameron and Grassie<sup>1</sup>, who used no added initiator for the copolymerization so that their result could not have been influenced by an effect arising from 'excess' of STL units adjacent to initiator fragments.

Direct application of the simplified copolymer composition equation to the results for polymers 1 and 2 leads to values of  $r_1$  (STY with STL) of 10 and 11 respectively; the value of  $r_1$  (STY with FSTL) is 7 (polymer 5), rather different from the value of 12 for polymer 6. In principle, the results for polymers prepared using BPO can be corrected for the end-of-chain STL or FSTL units. Consider polymer 6 to illustrate the

procedure. It is necessary to have information on the total incorporation of FSTL in the polymer, the average molecular weight, the average number of benzoate end-groups per polymer molecule and the value of  $k_{\text{FSTL}}/k_{\text{STY}}$  where  $k_{\text{FSTL}}$  and  $k_{\text{STY}}$  are the velocity constants for the reactions of FSTL and STY with the *p*-fluorobenzyloxy radical. Polymer 6 contains one FSTL for 75 STY units; its average degree of polymerization is about 350 so that the average polymer molecule contains 4.67 FSTL units. In the polymerizing system,  $[\text{FSTL}]/[\text{STY}]$  was  $16.10 \times 10^{-2}$ ; the value of  $k_{\text{FSTL}}/k_{\text{STY}}$  is taken as 10 so that

$$\frac{\text{no. of F.C}_6\text{H}_4\text{.CO.O.FSTL - end-groups}}{\text{no. of F.C}_6\text{H}_4\text{.CO.O.STY - end-groups}} = 1.61$$

If each polymer molecule has two *p*-fluorobenzoate end-groups, then the average polymer molecule has 1.23 FSTL units at end-of-chain sites and therefore 3.44 FSTL in-chain units. Accordingly,  $r_1$  is found to be 16 whereas a value of 12 was found from the total FSTL content of the polymer.

The results presented here indicate that, under some circumstances, caution may be necessary when considering the compositions of copolymers when one of the monomers is incorporated to only a small extent. Problems arise if the monomer which is comparatively unreactive in the growth reactions is very reactive towards the initiating species so that there is a marked tendency for it to be incorporated near chain-ends. More generally, there are difficulties for copolymers of rather low molecular weight if the relative reactivities of the monomers in initiation are quite different from their relative reactivities in the growth reactions.

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