Polymer Bulletin 34, 37–42 (1995)

Polymer Bulletin

Copolymerizations of various ring-fluorinated stilbenes with styrene

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Received: 18 August 1994/Revised version: 20 September 1994/Accepted: 25 September 1994

Summary

The E-isomers of 2-, 3- and 4-fluorostilbene and 4,4'-difluorostilbene and also the Z-isomers of 4-fluorostilbene have been examined as comonomers in the radical polymerization of styrene at 60°C. The low levels of incorporation of the fluoro-compounds have been measured by consideration of the 19F-NMR spectra of the copolymers, using fluorobenzene as an internal standard. The reactivities of the various fluorostilbenes towards the polystyrene radical are discussed and compared with those towards the benzoyloxy radical.

Introduction

A report (1) has already been given of a study of the reactions at 60°C of the E-isomers of 2-, 3- and 4-fluorostilbene (2-FSTL, 3-FSTL and 4-FSTL respectively) and the Z-isomer of the 4-substituted compound (Z4-FSTL); a similar examination has been made of the E-isomer of 4,4'-difluorostilbene (44-FSTL) (2). The work involved the use of benzoyl peroxide (BPO), labelled with both tritium and carbon-14, as initiator for a set of polymerizations of methyl methacrylate (MMA) in each of which one of the fluoro-compounds was present as a minor component. It was possible to determine for each polymer the ratio of the numbers of benzoate and phenyl end-groups derived from the initiator. The introduction of a FSTL into the polymerizing system led to a significant increase in the proportion of benzoate end-groups, explained in terms of the ready addition of the benzoyloxy radical to the FSTL. If k' and k" are respectively the rate constants for the decarboxylation of the benzoyloxy radical and the addition of the radical to the FSTL, k"/k' can be evaluated. The decarboxylation is taken as a reference reaction so that the values of k" for the fluorostilbenes can be compared.

The present paper refers to the reactions at 60°C of the polystyrene radical with ring-fluorinated derivatives of stilbene (STL). The derivatives were used as comonomers in polymerizations of styrene (STY) (monomer-1). The various monomer reactivity ratios, r_1, were evaluated so that the rate constants for the reactions of the FSTL's with the polySTY radical could be compared, taking the addition of STY to the radical as the reference reaction and considering the reciprocals of the values of r_1. The compositions of the copolymers were found through determinations of the fluorine contents by means of 19F-NMR with fluorobenzene as internal standard for both chemical shifts and F-contents. It was necessary to make a proper selection of the conditions for recording spectra to ensure valid comparison between peak areas and fluorine contents for the standard and the copolymers. This point was made previously (3) when 19F-NMR was applied for the determination of the fluorine atoms at chain-ends in the poly(aryl ether ether ketone) formed

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from a fluoroketone and resorcinol.

Copolymerizations of STY with the FSTL's were initiated by azobisisobutyronitrile (AIBN) rather than by BPO so as to avoid effects arising from "excess" FSTL units adjacent to benzoate end-groups formed in the process of initiation. Previous studies (4) of copolymerizations involving 4-FSTL depended upon the use of material labelled with carbon-14 and comparisons of the specific activities of the labelled 4-FSTL and the derived copolymers. Labelling with carbon-14 was applied similarly for examination of the copolymerization of STY with the E-isomer of STL; the results agreed well with those of Cameron and Grassie (5) who used STL labelled with tritium.

It should be pointed out that a related previous paper (1) contained an error in the Summary. The relative reactivities towards the benzoyloxy radical for MMA, the E-isomers of 2-, 3- and 4-fluorostilbene and the Z-isomer of 4-fluorostilbene are 1, 17, 18, 41 and 14 respectively, as in the text.

Experimental Methods and Calculations

Most of the materials were purified by standard procedures. The FSTL's were prepared by phase-transfer catalyzed Wittig reactions (6) as described previously (1).

Copolymerizations were performed anaerobically at 60°C using toluene as diluent; [STY] and [AIBN] were close to 2.80 and 2.00 $\times 10^{-2}$ mol dm^{-3} respectively. One copolymer was prepared using 44-FSTL with BPO as initiator. Reactions were monitored by dilatometry and conversions were less than 10%. Copolymers were recovered by precipitation in methanol, purified by two further precipitations from solutions in toluene and finally dried to constant weight in vacuum.

A test on the removal of free FSTL from copolymers was performed. A mixture of 64.8mg of pure polySTY and 77.9mg of 44-FSTL was dissolved in toluene; the mixture contained 9.6% by weight of fluorine. The polymer was recovered by precipitation in methanol and purified by a second precipitation from solution in toluene. Examination by 19F-NMR failed to detect any fluorine in the final product. Only two precipitations were used in this test whereas three precipitations were performed on the copolymers prepared in the presence of a FSTL; the result of the test can therefore be regarded as entirely satisfactory.

19F-NMR spectra were obtained at 93·7 MHz on a JEOL FX-100 spectrometer. Solutions of specimens were prepared in $CDCl_3$, using fluorobenzene as internal reference standard; the quantity of the standard was selected so that its fluorine content was similar to that of the specimen under examination. Measurements using proton noise decoupling were made, employing a modified 19F acquisition experiment in which the decoupling was gated off during a relaxation decay in order to permit complete decay of any induced nuclear Overhauser enhancements. In order to allow for total relaxation of the reference signal derived from a small mobile molecule, the interval between successive acquisitions was set at 20 s.

The method for determining the FSTL contents of the copolymers made using 2-, 3- or 4-FSTL can be summarized thus. Suppose that the specimen examined by 19F-NMR contains s mg of fluorobenzene and p mg of polymer and that (spectral area for standard)/(spectral area for copolymer) is R. The fractional weight of fluorine in the standard is 0.198 and so the corresponding quantity for the copolymer is given by $f = 0.198s/Rp$. The copolymer can be represented as $(C_8H_8)_n(C_{14}H_{11}F)_1$, the contributions of initiator fragments being negligible, and so $f = 19/(104n + 198)$. Putting together the two expressions for f leads to

$$n = \frac{0.923Rp}{s} - 1.9 \qquad (I)$$

A copolymer containing units derived from 44-FSTL can be represented as $(C_8H_8)_n(C_{14}H_{10}F_2)_1$; it can be shown that $f = 38/(104n + 216)$ and

$$n = \frac{1.846R_p}{s} - 2\cdot 1 \qquad \text{(II)}$$

Results

The 19F-NMR spectra of 2-, 3-, 4- and 44-FSTL consisted of single sharp peaks with chemical shifts (referenced to fluorobenzene $\delta = 0$) -4.89, -0.39, -1.18 and -1.08 ppm respectively. The spectrum for the specimen of Z4-FSTL showed a sharp peak at -1.63 ppm; it was accompanied by minor peaks due to fluorine-containing contaminants including 4-FSTL. The quantity of the E-isomer in the sample of Z4-FSTL was less than 5% by weight; it is insufficient to have any significant effect on the conclusions drawn here or in the previous paper (1).

The five FSTL's had no detectable effects on the rates of polymerization of STY. Examples of 19F-NMR spectra of their copolymers with STY are shown in Figure 1 which includes the reference signals for fluorobenzene except in spectrum (d). Units derived from 2-, 3- and 4-FSTL respectively gave rise to signals in the ranges -3.0 to -6.0, 0.5 to -2.5 and -3.5 to -5.5 ppm. For copolymers made using AIBN as initiator and 44-FSTL as comonomer, there were signals between -3.2 and -5.2 ppm; when BPO was used as initiator, there was an additional group of signals near -1 ppm attributed to 44-FSTL units adjacent to benzoate end-groups. The complexity of the spectra is due to alternative stereochemistries for the incorporated FSTL units and also, for the 2-, 3- and 4-isomers, to lack of regiospecificity in the addition of the FSTL to the polySTY radical. The spectrum of the polymer prepared using Z4-FSTL at quite high concentration ([STY]/[Z4-FSTL] = 18.4) was devoid of signals which could be attributed to incorporated Z4-FSTL.

For the copolymers prepared using 2-, 4- or 44-FSTL, the signals from the reference and the copolymer were completely separate so that the spectral areas could be compared without difficuly. For copolymers containing units derived from 3-FSTL, there was overlap of the signals. Spectrum (d) in Figure 1 was recorded without added fluorobenzene and refers to a copolymer prepared in the presence of 3-FSTL; the area upfield from -1.0 ppm is 40% of

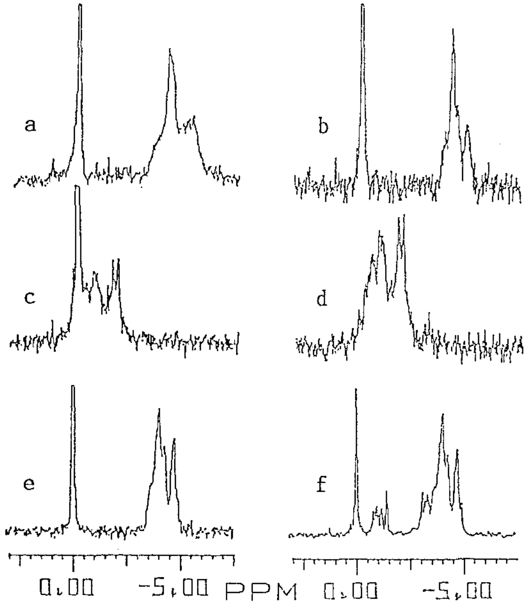

Figure 1. 19F-NMR spectra for copolymers of various FSTL's with STY.

(a) [STY]/[2-FSTL] = 11.6
(b) [STY]/[4-FSTL] = 32.5
(c) [STY]/[3-FSTL] = 18.0
(d) as for (c) but without fluorobenzene
(e) [STY]/[44-FSTL] = 34.6
(f) [STY]/[44-FSTL] = 40.1

(a)-(e), AIBN as initiator
(f) , BPO as initiator.

the total area. For copolymers prepared in the presence of 3-FSTL and for which spectra were recorded using fluorobenzene, for example (c) in Figure 1, the spectral areas upfield from -1.0 ppm were noted and then multiplied by 2.04 to give the complete areas for the copolymers; these areas were then subtracted from the total areas corresponding to all fluorine nuclei in the systems to give the areas due to the reference.

All the spectra were free from the sharp signals which would indicate the presence in the copolymer of occluded FSTL; it is possible however that any signal due to occluded 2-FSTL would have been obscured by signals from 2-FSTL chemically incorporated in the copolymer but the efficiency of the separation procedure, as reported in a previous section, makes this possibility very remote.

Information on typical systems is presented in Table 1; the selected examples are referred to in Figure 1. The complete final results were used to construct Figure 2. It is supposed that monomer reactivity ratio r_2 is close to zero and that, in each case, [STY] is much larger than [FSTL] in the feed. It appears that the simplified form of the copolymer composition equation

$$\frac{(STY)}{(FSTL)} = \frac{r_1\,[STY]}{[FSTL]} + 1$$

is satisfied for the four cases. From the least squares plots, the derived values of r_1 for 2-, 3-, 4- and 44-FSTL are 17.7, 8.0, 9.3 and 9.3 respectively; it is considered that they are subject to uncertainties not exceeding ± 10%.

Discussion

Relative values of k" for the reactions with the benzoyloxy radical of MMA, STY, 2-, 3-, 4-, Z4- and 44-FSTL are 1, 8, 17, 18, 41, 14 and 53 respectively. It is apparent that the 2-, 3- and Z4-isomers have similar reactivities towards the radical and that they are appreciably less reactive than

Table 1. Copolymerizations of ring-fluorinated stilbenes with styrene

comonomer	[STY]/[FSTL] in feed	mg copolymer for NMR	ratio of (a) spectral areas	(STY)/(FSTL) calc. for copolymer
2-FSTL	11.6	136 (b)	1.30	213
3-FSTL	18.0	80 (b)	1.90 (d)	183
4-FSTL	32.5	80 (c)	1.63	307
44-FSTL	34.6	90 (b)	0.75	317

(a) - (area for fluorobenzene)/(area for copolymer)
(b) - used with 0.76 mg of fluorobenzene; (c) - with 0.39 mg
(d) - found by indirect method - see the text

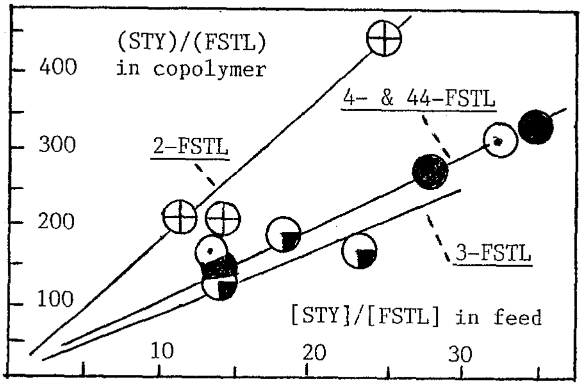

Figure 2. Plots of (STY)/(FSTL) in copolymer vs. [STY]/[FSTL] in feed.

⊕ 2-FSTL
◔ 3-FSTL
⊙ 4-FSTL
● 44-FSTL

the 4- and 44- isomers. For STL itself(7), the relative value of k" is 48 i.e. not greatly different from the corresponding quantities for 4- and 44-FSTL. The relative values of k" for some other halogenated derivatives of STL, viz. 4-chlorostilbene (4-CSTL) and 4,4'-dichlorostilbene, are 50 and 47 respectively (2). The result for 4-CSTL differs significantly from the value of 90 quoted previously (7). The older value may not be reliable; it came from work depending upon the study by 13C-NMR of benzoate end-groups, derived from 13C-enriched BPO, in copolymers of MMA with 4-CSTL. The spectra were recorded on an instrument operating at comparatively low field and at the limit of its sensitivity. It is concluded that the introduction of fluorine or chlorine at the 4-position or at the 4,4'-positions in STL has only a small effect on the reactivity towards the benzoyloxy radical.

The relative reactivities towards the polySTY radical, as deduced from studies of binary copolymerizations involving STY, are 1, 0.06, 0.12, 0.11 and 0.11 for STY, 2-, 3-, 4- and 44-FSTL respectively and that of Z4-FSTL is close to zero; the corresponding quantity for STL is 0.09 (4,5). It appears therefore that the E-isomers of the various FSTL's are not greatly different from STL in their reactivities towards the polySTY radical.

There are distinct differences between the patterns of reactivity for the FSTL's towards the two reference radicals being considered. In all cases the compounds are rather reactive towards the benzoyloxy radical but comparatively inert towards the polySTY radical; this difference is particularly evident for Z4-FSTL. Both 2- and 3-FSTL are significantly less effective than 4- and 44-FSTL in capturing the benzoyloxy radical; for reaction with the polySTY radical, however, 3-FSTL closely resembles 4- and 44-FSTL but 2-FSTL is less reactive by a factor of about two. It is perhaps possible that the lower reactivity of 2-FSTL results from steric hindrance caused by the presence of a fluorine atom at the 2-position in one of the phenyl rings.

It would be interesting to have information on the reactivities in radical polymerizations of ring-fluorinated derivatives of STY but no relevant publication has been traced although the 2-, 3- and 4-fluoro derivatives of STY are on sale. Knebelkamp and Heitz (8) have reported on the syntheses and properties of poly(α-fluorostyrene)s, including the 2- and 4-fluoro-derivatives. Under some circumstances, these polymers readily undergo dehydrofluorination involving the fluorine atoms directly attached to the carbon atoms of the main chains; in this respect, they differ profoundly from what would be expected for ring-fluorinated polySTY and for polySTY containing units derived from a FSTL. There was a pronounced tendency for the poly(α-fluorostyrene)s having substituents at the 2-position to yield polymers with quite low molecular weights and comparatively high glass transition temperatures. These findings suggest that fluorine at the 2-position in the phenyl group of STY, or in one of the phenyl groups of STL, can produce quite significant effects.

Herman and Teyssié (9) pointed out that the electronic situation in monomers such as STY can be assessed by 13C-NMR studies. No direct information is available at present for the derivatives of STL but it is relevant that the 19F chemical shift for 2-FSTL is notably larger than those for the other FSTL's. It can be argued that an influence of the olefinic bond upon the 19F NMR spectrum for a FSTL must be accompanied by an effect of the fluorine on the olefinic bond and that, in this respect, 2-FSTL is quite different from the other FSTL's.

It is plain that the factors governing the reactivities of the various FSTL's towards the oxygen-centred benzoyloxy radical differ from those which affect their reactivities towards the polySTY radical. Another point emerging from this work is the confirmation of the applicability of 19F-NMR for study of small contents of fluorine-containing groups in high polymers; this feature was shown previously for fluorobenzoate and fluorophenyl end-groups derived from 4-fluorobenzoyl peroxide (10) and for terminal fluorine atoms in certain condensation polymers (3).

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