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Effects of Substituents in Stilbene Upon Its Reactivity in Radical Polymerizations

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Summary

Polymerizations of methyl methacrylate and styrene have been performed in the presence of the *cis* and *trans* isomers of 4-methoxy-4'-chlorostilbene (SSTL) using as initiators benzoyl peroxide and 2-cyano-2-propylazoformamide, both enriched with carbon-13. ^{13}C-NMR spectra of the polymers show that SSTL units are present at many of the sites adjacent to benzoate end-groups but not to a detectable extent at sites adjacent to 2-cyano-2-propyl end-groups. The presence of the substituents in the molecule of stilbene greatly enhances its reactivity towards the benzoyloxy radical.

Introduction

Attempts to copolymerize *trans*stilbene (tSTL) with methyl methacrylate (MMA) or styrene (STY) have apparently failed (1,2) but, when benzoyl peroxide (BPO) is used as the initiator, the resulting polymers contain appreciable numbers of the end-group $C_6H_5.CO.O.STL\sim$ (3). These STL units correspond to only low concentrations in the whole polymers but their presence indicates that tSTL reacts readily with the radical $C_6H_5.CO.O$. If BPO is replaced by azobis(isobutyronitrile) (AIBN) or 2-cyano-2-propylazoformamide (AZOF), the polymers contain no detectable $(CH_3)_2C(CN)$.STL-groups; evidently there is no significant reaction of tSTL with $(CH_3)_2C(CN)$. radicals. These conclusions about end-groups were reached from work involving the use of BPO enriched in its carbonyl groups with carbon-13 (^{13}C-BPO) and also AIBN and AZOF containing $^{13}CH_3$ groups (referred to as ^{13}C-AIBN and ^{13}C-AZOF). The environments of the initiator fragments incorporated in polymers were examined by ^{13}C-NMR spectroscopy; the chemical shifts associated with isotopically enriched end-groups depend upon the natures of the attached units (4).

The investigations have been extended to a derivative of STL, viz. 4-methoxy-4'-chlorostilbene. It was expected that an electron-repelling substituent in one ring and an electron-attracting substituent in the other might cause substantial modification of the reactivity towards radicals. Samples of the *cis* and *trans* isomers of the substituted stilbene (referred to as cSSTL and tSSTL respectively) were used separately.

Experimental

SSTL was prepared by a phase transfer catalyzed Wittig reaction using *p*-methoxybenzyltriphenylphosphonium chloride and *p*-chlorobenzaldehyde (5). The crude product was dissolved in methanol from which tSSTL was crystallized. The mother liquor was evaporated and the residue was treated with petrol; the insoluble triphenylphosphine was filtered off. The solvent was evaporated and cSSTL was then distilled. The isomers were obtained at yields between 45 and 50%; the spectral characteristics and elemental analyses were consistent with the expected structures. Other materials were purified by standard procedures. Preparations of ^{13}C-enriched initiators have been described (4,6). Polymerizations were performed with toluene as diluent under air-free conditions. Polymers were recovered by precipitation in methanol, purified by reprecipitation and finally dried in vacuum. ^{13}C-NMR spectra were recorded for $CDCl_3$ solutions at ambient temperature using a JEOL FX100 Fourier-transform spectrometer operating at 25.05 MHz (4).

Results and Discussion

Polymerizations of MMA at approx. 2 mol/l were initiated at 100°C by ^{13}C-AZOF at approx. 3g/l. The ^{13}C-NMR spectra of polymers prepared in the presence of tSSTL or cSSTL at about 0.2 mol/l could not be distinguished from that of a polymer prepared in the absence of SSTL; evidently neither isomer entered polymer to an extent detectable by ^{13}C-NMR. There were signals characteristic of the group $(CH_3)_2C(CN)$.MMA- but none which could be attributed to initiator fragments attached to SSTL units.

Similar polymerizations were initiated at 60°C with ^{13}C-BPO at approx. 2.5 g/l. Again, incorporation of SSTL in polyMMA could not be detected directly by ^{13}C-NMR (note the absence of signals in the region 120-140δ in spectrum A of Figure 1); the signals due to C_6H_5.CO.O-end-groups in polymers were however modified as a result of the presence of cSSTL or tSSTL in the polymerizing system (compare the signals around 165δ in spectra B, C and D of Figure 1). Benzoate groups attached to polyMMA chains give signals at 165.80 and 165.65δ; these signals diminish with increase of [tSSTL] or [cSSTL] in the reaction system while there is growth of a signal at 165.25δ attributed to benzoate groups attached to SSTL units.

In the case of tSSTL, the areas under the peaks for the two types of end-groups can be related to the relative numbers of these groups and to the rates of the reactions of the primary radical:

$$\frac{\text{area for } C_6H_5.CO.O.SSTL\text{-}}{\text{area for } C_6H_5.CO.O.MMA\text{-}} = \frac{\text{no. of } C_6H_5.CO.O.SSTL\text{-groups}}{\text{no. of } C_6H_5.CO.O.MMA\text{-groups}}$$

$$= \frac{k_1[tSSTL]}{k_2[MMA]} \qquad (I)$$

where k_1 and k_2 are the velocity constants for the reactions of C_6H_5.CO.O. with tSSTL and MMA respectively. In corresponding equations for other systems, k_1', k_3 and k_4 refer to reactions of C_6H_5.CO.O. with cSSTL, STY and tSTL respectively. The ratio of the areas under the peaks due to the end-groups cannot be determined precisely but, from spectra such as those in Figure 1, approximate values of k_1/k_2 and k_1'/k_2 are 230 and 70 respectively.

Experiments with STY in place of MMA gave generally similar results; the chemical shift for the signals associated with the end-group C_6H_5.CO.O.STY- was about 166.2δ. Use of a relationship corresponding to I leads to k_1/k_3=70 and k_1'/k_3=25. Values of 40 and 7 have been given (3) for k_4/k_2 and k_4/k_3 respectively for systems involving tSTL.

By comparing k_1/k_2 with k_4/k_2 and k_1/k_3 with k_4/k_3, approximate values of k_1/k_4 are found as 6 (using MMA for reference) and 10 (using STY for reference). The agreement is poor but plainly the reactivity of STL towards C_6H_5.CO.O. can be greatly affected by substitution. Comparisons

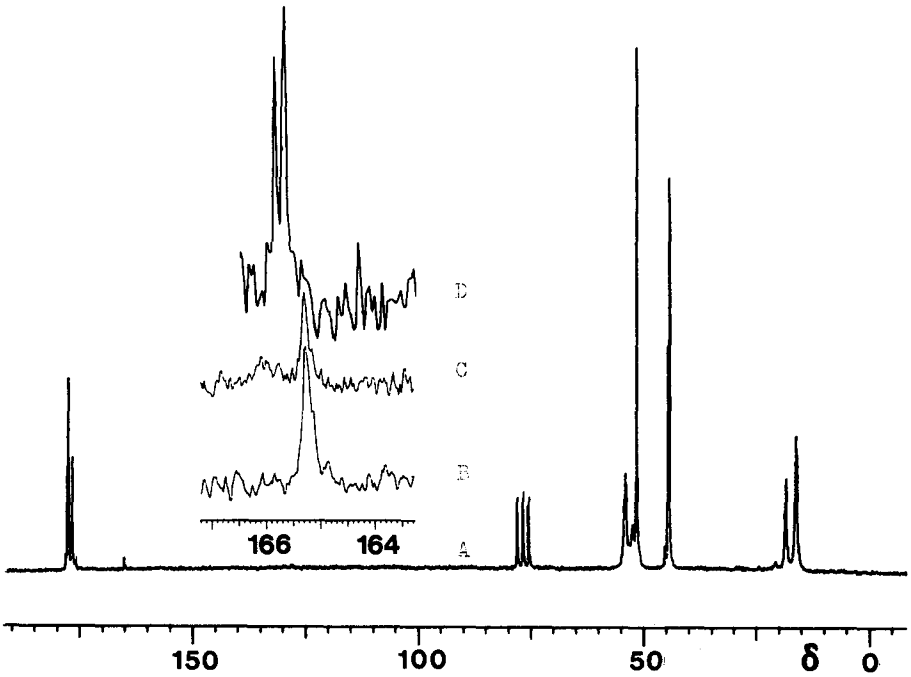

Figure 1. ^{13}C-NMR spectra of polymers prepared with ^{13}C-BPO. Feeds, [tSSTL]/[MMA]=0.054 (A & B), 0.010 (C), 0 (D).

of k_1/k_2 with k_1'/k_2 and k_1/k_3 with k_1'/k_3 show that tSSTL is about 3 times as reactive as cSSTL towards $C_6H_5.CO.O.$. A similar difference has been found for isomers of STL in radical reactions (7,8) and attributed to greater stability of the transition state for the reaction of the more stable trans isomer, leading to a lowering of the activation energy.

Comparisons of k_1/k_2 and k_1/k_3, k_1'/k_2 and k_1'/k_3, and k_4/k_2 and k_4/k_3 give values of 3, 3 and 6 respectively for k_3/k_2 at 60°C; the agreement is poor but clearly STY is confirmed as more reactive than MMA towards $C_6H_5.CO.O.$. When decarboxylation of the primary radical is used for reference to compare the reactivities of the monomers (9), $k_3/_2$ is found to be 8; this result is regarded as reliable being consistent with data for a variety of systems. In the present study, large errors can arise from uncertainties about areas in NMR spectra but it is necessary to consider other difficulties also.

The ^{13}C-NMR characteristics for the carbonyl carbon atoms in $C_6H_5.CO.O.SSTL$-, $C_6H_5.CO.O.STL$- and $C_6H_5.CO.O.CH(C_6H_5).CH_2$- are very similar. The peaks attributed to $C_6H_5.CO.O.SSTL$- at about 165.25δ may therefore include contributions from benzoate groups attached "abnormally" to STY units either by head-addition of a primary radical or by primary radical termination (10). If this is so, k_1/k_3 and k_1'/k_3 are overestimated; if the values of k_1/k_2 and k_1'/k_2 are regarded as essentially correct, then k_3/k_2 must be underestimated. This effect however must be quite small and it could not account by itself for a value of k_3/k_2 which is low by a factor of at least 2.

In principle, addition of $C_6H_5.CO.O.$ to tSSTL or cSSTL can occur at either end of the double bond to give two distinct radicals; these products might not be equally efficient in reactions with monomeric MMA and STY. It is possible to construct speculative schemes according to which k_3/k_2 would be underestimated by a factor of 2 or more in experiments involving tSSTL or cSSTL; experimental tests are feasible and work is in progress. The present results, even with their limitations, show that the reactivity of stilbene towards $C_6H_5.CO.O.$ can be greatly changed by substitution in the rings and that it is possible to prepare polymers containing high proportions of benzoate end-groups attached to stilbene-type residues.

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