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The reaction of beta-methylstyrene with the benzoyloxy radical

C.A. Barson[1], J.C. Bevington[2*], and T.N. Huckerby[2]

[1]School of Chemistry, The University, Birmingham B15 2TT, U.K.
[2]Department of Chemistry, The University, Lancaster LA1 4YA, U.K.

Summary

Benzoyl peroxide, either labelled with carbon-14 and tritium or enriched with carbon-13, has been used to initiate polymerizations of methyl methacrylate containing β-methylstyrene. Studies of the end-groups derived from the initiator show that at 60°C β-methylstyrene is about twice as reactive as styrene or α-methylstyrene towards the benzoyloxy radical. The incorporation of β-methylstyrene in polymer is small but its concentration at sites adjacent to benzoate end-groups may be quite high.

Introduction

The E-isomers of stilbene and related compounds are very effective in capturing the benzoyloxy radical but they react only sluggishly with carbon centred radicals such as the 1-cyano-1-methylethyl radical derived from azobisisobutyronitrile (AIBN) or the growing radicals present during the polymerizations of monomers such as styrene or methyl methacrylate (MMA). Consequently the presence of say stilbene during the polymerization of a monomer such as MMA, initiated by benzoyl peroxide (BPO), can lead to polymer in which many of the benzoate end-groups are attached to units derived from stilbene although the total incorporation of that substance is slight; the effect is not found if BPO is replaced by AIBN (1). Similar effects are found if 1,4-diphenylbutadiene is used instead of stilbene (2). The attachment of the benzoyloxy radical to an olefinic carbon atom carrying an aromatic group occurs also in the case of styrene and there is some head-addition of the radical to that monomer, as first shown by Moad et al. (3).

Studies of additions of the benzoyloxy radical to unsaturated compounds have now been extended to β-methylstyrene (BMST) which ordinarily does not form homopolymers and is unreactive as a comonomer in radical polymerization. Otsu (4) has referred to the low reactivity in radical polymerization of most β-substituted acrylic derivatives although dialkyl fumarates and some related compounds (but not dialkyl maleates) undergo radical polymerization. The case of acenaphthylene, as another α,β-substituted olefin, should be mentioned; its ready participation in radical polymerization is connected with strain in the five-membered ring, relieved by opening of the carbon-carbon double bond (5).

Two experimental procedures have been developed for study of the reactivities towards the benzoyloxy radical of unsaturated substances which do not form homopolymers by polymerizations initiated by BPO. One method involves determination of the relative numbers of benzoate and phenyl end-groups in polymers of MMA, prepared using BPO as initiator in the presence of a substance such as BMST (6); for this purpose, use is made of peroxide suitably labelled with both carbon-14 and tritium ($^{14}C,^{3}H$-BPO). The other method (1) requires the use of ^{13}C-enriched peroxide (^{13}C-BPO) and depends upon the

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*Author for correspondence

examination of polymers by ^{13}C-NMR for direct comparison of the numbers of benzoate end-groups attached to units derived from MMA and the numbers adjacent to units derived from the other unsaturated substance.

Experimental

Procedures and materials were generally as described previously (1,6). The E- (or trans-) isomer of BMST (Aldrich) was redistilled under N_2 at reduced pressure; its identity and purity were confirmed by GC/MS.

Polymerizations were performed at 60°C under air-free conditions and were allowed to proceed to approx. 8% conversion. Polymers were recovered by precipitation in methanol and purified by two further precipitations. Radioactive materials were assayed using an LKB Wallac "Spectral" 1219 Liquid Scintillation Counter; ^{13}C-NMR spectra were recorded at 100 MHz on a Bruker WH400 instrument.

Results and Discussion

For a set of polymerizations, the concentrations of MMA and BPO were close to 3.10 and 0.67×10^{-2} mol dm^{-3} respectively. Introduction of BMST into the system caused reduction in the rate of polymerization measured dilatometrically; for example replacement of 20% of the toluene used as diluent by BMST, to make the concentration of the latter 1.01 mol dm^{-3}, caused the rate of contraction to decrease by 68%. Similar effects were observed when AIBN was used as initiator instead of BPO.

A polymer prepared from a system in which $[BMST]/[MMA]$ was 0.41, using AIBN as initiator, was purified by reprecipitation from dimethylformamide rather than toluene and then examined by ^{13}C-NMR. There were only very faint signals attributable to aromatic carbon atoms and it was deduced that less than one BMST unit was incorporated for 50 units of MMA. The low reactivity of BMST as a comonomer is therefore confirmed. Its effect on the overall rate might be explained in terms of degradative transfer and the production of the substituted allylic radical $\cdot CH_2 \cdot CH{:}CHPh$.

Polymerizations of MMA in toluene containing BMST were initiated by $^{14}C,^{3}H$-BPO for which (^{3}H-activity)/(^{14}C-activity) was 1.35; details are given in Table 1. For each polymer, the value of (no. of PhCOO- end-groups)/(no. of Ph- end-groups) is expressed as x/(1-x); x is found by means of the relation

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

The results are used with the equation (6)

$$\frac{x}{(1-x)[MMA]} = \frac{k_2}{k_1} + \frac{k_2'[BMST]}{k_1[MMA]}$$

where k_1 is the rate constant for the decarboxylation of the benzoyloxy radical and k_2 and k_2' are those for the reactions leading to attachment of the radical to MMA and BMST respectively.

Table 1. Polymerizations using radioactive BPO

[MMA] mol dm^{-3}	[BMST] mol dm^{-3}	(^{3}H-activity)/(^{14}C-activity) of polymer	derived value of x
1.85	0.15	2.34	0.577
3.10	0.53	1.75	0.771
1.78	0.44	1.89	0.714
3.10	1.01	1.64	0.823

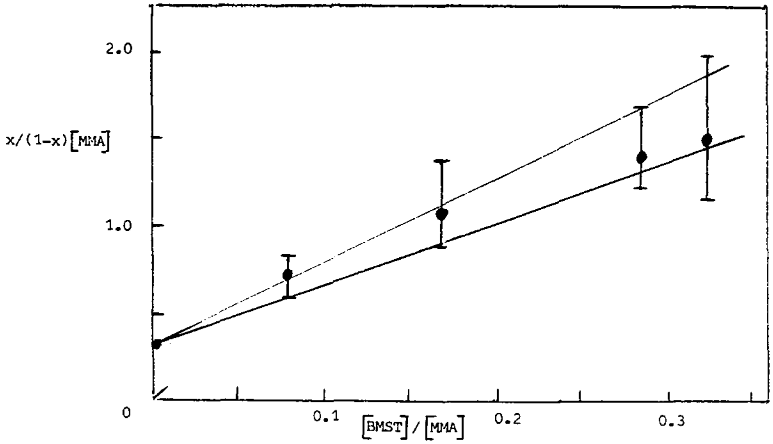

Figure 1. Plot showing variation of (no. of PhCOO- end-groups)/(no. of Ph- end-groups) in polyMMA with concentration of BMST in the polymerizing system.

In Figure 1, the error bars correspond to ±5% uncertainties in the values of x; it can be seen how sensitive the quantity $x/(1-x)[MMA]$ is to error especially when x is appreciably greater than 0.5. The value of k_2/k_1 is taken as 0.31 mol^{-1} dm^3. The lines as drawn lead to values of 3.5 and 4.8 mol^{-1} dm^3 for k_2'/k_1 indicating that k_2/k_2' is probably between 0.089 and 0.065.

MMA was polymerized using ^{13}C-BPO in the presence of BMST; the value of [BMST]/[MMA] was 0.174. The ^{13}C-NMR spectrum of the resulting polymer is to be compared with that of a polymer prepared similarly but in the absence of BMST. The parts of the spectra shown in Figure 2 include the signals arising from the enriched carbonyl carbon atoms in benzoate end-groups. The very evident difference between the spectra can be reasonably interpreted by supposing that many of the benzoate end-groups in polymer (a) are adjacent to units derived from BMST.

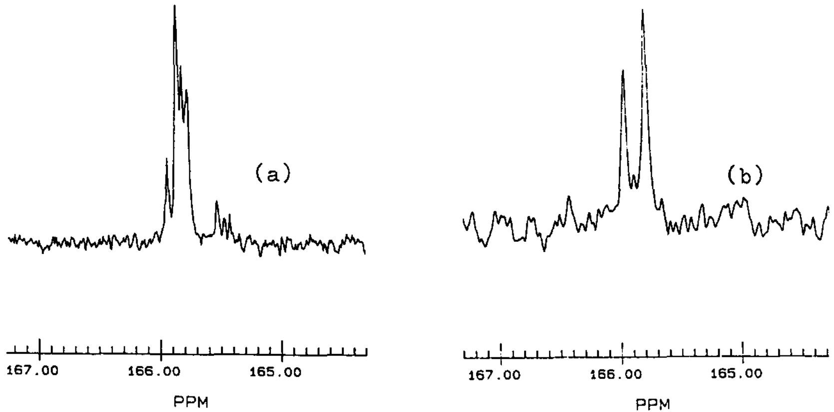

Figure 2. Parts of the ^{13}C-NMR spectra of polyMMA samples prepared using ^{13}C-BPO. (a) BMST present during polymerization; (b) no additive.

The peak at 165.95 ppm in spectrum (a) seems to match the downfield peak in spectrum (b). This peak in spectrum (b) covers an area which is about 40% of the total area corresponding to benzoate end-groups. It is convenient to consider three fairly well resolved regions in spectrum (a), viz. (i) 165.9 to 166.0 ppm (ii) 165.7 to 165.9 ppm and (iii) 165.4 to 165.7 ppm. The approximate relative areas covered by the peaks in regions (i), (ii) and (iii) are 1, 9 and 1 respectively. It is believed that (i) contains only signals from Ph.CO.O.MMA- end-groups, that (ii) includes the upfield component for those end-groups and also some of the signals from benzoate end-groups attached to units derived from BMST and that signals in (iii) are due entirely to end-groups adjacent to BMST units.

By combining information derived from spectra (a) and (b), it is found that

$$\frac{\text{area for Ph.CO.O.MMA- groups}}{\text{area for Ph.CO.O.BMST- groups}} = \frac{A}{A'} = \frac{100/40}{9 - 60/40 + 1} = 0.29$$

Consideration of the competition between MMA and BMST for capture of benzoyloxy radicals leads to the relationship (1)

$$\frac{A}{A'} = \frac{\text{no. of Ph.CO.O.MMA- groups}}{\text{no. of Ph.CO.O.BMST- groups}} = \frac{k_2[\text{MMA}]}{k_2'[\text{BMST}]}$$

from which k_2/k_2' is found to be 0.05.

The two sets of signals assigned to benzoate end-groups adjacent to BMST units may correspond to the groups Ph.CO.O.CHMe.CHPh- and Ph.CO.O.CHPh.CHMe-. Consideration of stabilities of the products from the reactions of Ph.CO.O. with BMST suggests that the former type of end-group is likely to be the more abundant and therefore associated with the signals in spectral region (ii). Extension of the treatment in the previous paragraph indicates that the relative numbers of the two types of end-group are ~ (9-1.5) and 1 i.e. approx. 7.5 and 1. Moad et al. (3) showed that the benzoate end-group attached to the head of a styrene unit gives a ^{13}C-NMR signal upfield from that for the more abundant end-group produced by tail-addition of the benzoyloxy radical to styrene. This finding can be regarded as further evidence that the signals between 165.4 and 165.7 ppm in spectrum (a) of Figure 2 arise from attachment of the benzoyloxy radical to the carbon atom with a phenyl group; it will however require the examination of suitable model compounds to test this view.

The two values of k_2/k_2' are not in close agreement but they are similar and it must be noted that, for both procedures, errors are very likely. In applying the procedure involving ^{14}C, ^{3}H-BPO, it is assumed that the value of k_1 is not affected by introduction of BMST into the polymerizing system. Of the additives so far examined, only cinnamic acid appears to affect significantly the decarboxylation of the benzoyloxy radical, the evidence being a gross discrepancy between the results obtained by the two procedures (7). The use of radioactive BPO appeared to show that cinnamic acid is quite effective in capturing the benzoyloxy radical whereas the experiments with ^{13}C-BPO gave no indication of benzoate end-groups attached to units derived from the unsaturated acid; the difference could be explained readily by supposing that decarboxylation of the benzoyloxy radical is made much less likely by the presence of cinnamic acid i.e. k_1 is reduced. It is clear that any such effect must be small in the case of BMST.

The approximate relative reactivities towards the benzoyloxy radical of MMA, styrene, α-methylstyrene, BMST, α-methylstilbene and αβ-dimethylstilbene are 1, 8, 9, 16, 51, 28 and 2.4 respectively. Particularly high reactivity is found for those substances in which both carbon atoms of the central olefinic bond carry phenyl groups although the additional presence of a methyl group on one or both of these carbon atoms causes reduction in reactivity, presumably because of a steric effect; in the case of the dimethylstilbene, the reactivity is reduced to quite a low level. It seems surprising that BMST should be as much as twice as reactive as styrene and α-methylstyrene towards the benzoyloxy radical; further studies are being made on the reactivities of other unsaturated substances of the general formula $CH_3.CH:CHX$.

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