The reactivity towards the benzoyloxy radical of 1,4-bis(2-methylstyryl)benzene

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It has been found that 1,4-bis(2-methylstyryl)benzene (MSB) is ~520 times as effective as methyl methacrylate in capturing the benzoyloxy radicals generated at 60°C by dissociation of benzoyl peroxide. This result has been obtained from examinations of the end groups in samples of poly(methyl methacrylate) prepared using benzoyl peroxide as initiator in the presence of MSB at low concentrations.

(Keywords: 1,4-bis(2-methylstyryl)benzene; methyl methacrylate; benzoyl peroxide; radical polymerization; end groups)

INTRODUCTION

Stilbene (STL) and 1,2-diphenylpropene are very effective in capturing the benzoyloxy radical but 1,3-diphenylpropene is much less reactive towards it[1]. The reactivity of 1,4-diphenylbuta-1,3-diene (DPB) towards the benzoyloxy radical is high and considerably greater than those of 2,3-diphenylbuta-1,3-diene and conjugated dienes not containing aryl groups[2]. High reactivities have been found also for those analogues of STL and DPB in which one or both phenyl groups are replaced by other aryl groups[3,4]. It appears therefore that substances possessing high reactivity towards the radical have structures such that the carbon atom to which the radical becomes attached carries an aromatic ring and there is extensive conjugation through the molecule. These conditions are satisfied in the case of 1,4-bis-styrylbenzene, $\mathrm{Ph{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}Ph}$, which can be regarded as being related to STL and DPB. Compounds of this type are being examined with respect to reactivity towards the benzyloxy radical and the first experiments have been performed with 1,4-bis(2-methylstyryl)benzene (MSB). The procedures depend upon analyses for the end groups in polymers of methyl methacrylate (MMA), made at 60°C using benzoyl peroxide (BPO) as initiator in the presence of MSB. Comparisons are made between the rate constants for the additions of the benzoyloxy radical to the substance under examination and to MMA. For some of the substances, the rate constant is several hundred times that for the reaction involving MMA.

When BPO is used to initiate polymerization in a mixture of unsaturated substances M_a and M_b, the following scheme should be considered in connection with the formation of end groups derived from the peroxide.

$$(\mathrm{Ph{\cdot}CO{\cdot}O})_2 \rightarrow 2\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}}$$

$$\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} \rightarrow \mathrm{Ph{\cdot}} + \mathrm{CO_2} \quad \text{rate constant} = k_1 \qquad (1)$$

$$\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} + \mathrm{M_a} \rightarrow \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}M_a{\cdot}} \qquad k_{2a} \qquad (2a)$$

$$\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}} + \mathrm{M_b} \rightarrow \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}M_b{\cdot}} \qquad k_{2b} \qquad (2b)$$

$$\mathrm{Ph{\cdot}} + \mathrm{M_a} \rightarrow \mathrm{Ph{\cdot}M_a{\cdot}} \qquad (3a)$$

$$\mathrm{Ph{\cdot}} + \mathrm{M_b} \rightarrow \mathrm{Ph{\cdot}M_b{\cdot}} \qquad (3b)$$

It is supposed that benzoate groups are incorporated in the polymer only by reactions 2a and 2b. A fraction x is defined as (no. of benzoate end groups)/(sum of benzoate and phenyl end groups) and the relationship:

$$x/(1-x) = k_{2a}[\mathrm{M_a}]/k_1 + k_{2b}[\mathrm{M_b}]/k_1 \qquad (4)$$

can be derived if it is supposed that all phenyl radicals produced in reaction 1 subsequently enter the polymer by reactions 3a or 3b or by other processes. According to the scheme shown above, two types of benzoate end groups are formed, from reactions 2a and 2b; consideration of these competing reactions leads to the relationship:

$$\frac{\text{no. of } \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}M_a}\text{– end groups}}{\text{no. of } \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}M_b}\text{– end groups}} = \frac{k_{2a}[\mathrm{M_a}]}{k_{2b}[\mathrm{M_b}]} \qquad (5)$$

The use of doubly labelled BPO, having ^{14}C at its carbonyl sites and tritium in its rings ([^{14}C, ^{3}H]BPO), allows determination of the fraction x as:

$$\frac{^{14}\text{C activity of polymer}}{^{14}\text{C activity of peroxide}} \times \frac{^{3}\text{H activity of peroxide}}{^{3}\text{H activity of polymer}}$$

Assays of polymers derived from systems in which $[\mathrm{M_a}]$ and $[\mathrm{M_b}]$ have various values, calculations of the values of x and then application of equation (4) lead to evaluation of k_{2a}/k_1 and k_{2b}/k_1; the reactivities of unsaturated substances towards the benzoyloxy radical can then be compared using the decarboxylation of the radical for reference.

An alternative procedure depends upon the use of BPO enriched with ^{13}C at its carbonyl sites ([^{13}C]BPO) and

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examination by ^{13}C n.m.r. of the polymers derived from mixtures of M_a and M_b. In general, it is possible to distinguish between the signals arising from the benzoate groups attached to units of different types. Provided that adequate relaxation conditions are used, equation (5) can be modified to

$$\frac{\text{Spectral area for Ph}\cdot\text{CO}\cdot\text{O}\cdot\text{M}_a-\text{ end groups}}{\text{Spectral area for Ph}\cdot\text{CO}\cdot\text{O}\cdot\text{M}_b-\text{ end groups}}=\frac{k_{2a}[\text{M}_a]}{k_{2b}[\text{M}_b]} \quad (6)$$

so that k_{2a}/k_{2b} can be determined without reference to the decarboxylation of the radical.

EXPERIMENTAL

MSB (Lancaster Synthesis) was recrystallized from a mixture of toluene and methanol. [^{14}C, ^{3}H]BPO, [^{13}C]BPO and BPO labelled in its rings with ^{14}C ([^{14}C]BPO) were prepared from the appropriate benzoic acids through benzoyl chloride. The specific activities of [^{14}C, ^{3}H]BPO were 4.83×10^5 and 6.28×10^5 Bq g^{-1} for ^{14}C and ^{3}H, respectively, and that of [^{14}C]BPO was 8.50×10^5 Bq g^{-1}. The enrichment of [^{13}C]BPO was close to 50%.

Polymerizations were performed at 60°C under air-free conditions with MMA at 3.10 mol dm^{-3} in toluene and the peroxide at a concentration close to 0.62×10^{-2} mol dm^{-3}. Reactions were monitored dilatometrically and conversions did not exceed 10%. Polymers were recovered by precipitation in methanol and purified by two reprecipitations from solutions in toluene.

Radioactive assays were performed by liquid scintillation counting of solutions using an LKB 'Spectral' liquid scintillation counter. ^{13}C n.m.r. spectra were recorded at 100 MHz using a Bruker WH4000 spectrometer.

RESULTS AND DISCUSSION

The rate of polymerization of MMA under the specified conditions was only slightly reduced when MSB was present at the concentrations used in this study. In a set of experiments, [^{14}C]BPO was used as initiator so that it was possible to discover whether the total rate of incorporation of initiator fragments in polymer was affected by the presence of MSB. A polymer of MMA prepared using BPO can be represented by the empirical formula $(C_6H_5\cdot CO\cdot O)_x(C_6H_5)_{1-x}(C_5H_8O_2)_n$. If the peroxide is labelled in its rings with ^{14}C, n can be taken as 121(specific activity of peroxide)/100(specific activity of polymer). The rate of incorporation of initiator fragments (R_{inc}) is then given by (rate of polymerization)/n. Two polymers of MMA, made under the specified conditions using [^{14}C]BPO, had specific activities of 5.19×10^2 and 5.58×10^2 Bq g^{-1} so that the average of the values of n was 1917; the specific activity of a polymer made similarly but in the presence of MSB at 0.94×10^{-2} mol dm^{-3} was 5.87×10^2 Bq g^{-1} corresponding to n being 1756. The rate of polymerization when MSB was present was 90% of that in the cases where it was absent so that any effect of MSB on R_{inc} must have been very small.

[^{14}C, ^{3}H]BPO was used to initiate polymerizations of MMA under the standard conditions. For concentrations of MSB of 0.63×10^{-2} and 1.27×10^{-2} mol dm^{-3}, the values of (^{3}H activity)/(^{14}C activity) for the resulting polymers were 1.91 and 1.66, respectively, to be compared with 1.30 for the peroxide and leading to values of x of 0.681 and 0.783. For application of equation (4), k_2/k_1 for MMA is taken as 0.31 mol^{-1} dm^3 corresponding to a value of 0.490 for x for a polymer of MMA formed from monomer at 3.10 mol dm^{-3} in the absence of MSB or similar additive. The values of k_2/k_1 for MSB are found to be 186 and 208 mol^{-1} dm^3. The results are very sensitive to small changes in x; variations of up to $\pm 5\%$ lead to values of k_2/k_1 for MSB in the ranges 138–246 and 154–288 mol^{-1} dm^3, corresponding to 445–794 and 497–929 for $k_{2,\text{MSB}}/k_{2,\text{MMA}}$.

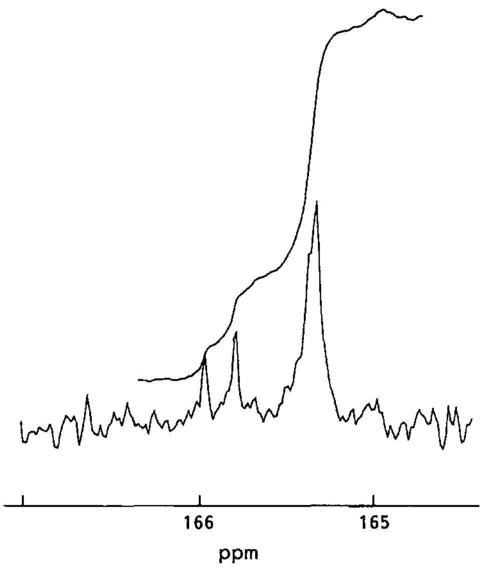


Figure 1 Part of the 100 MHz ^{13}C n.m.r. spectrum for a polymer recovered from a system in which [1,4-bis(2-methylstyryl)benzene]/[methyl methacrylate] was 0.53×10^{-2} and [^{13}C]BPO was used as initiator at 60°C

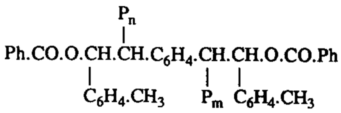
Figure 1 shows part of the ^{13}C n.m.r. spectrum of poly(methyl methacrylate) made under the standard conditions using [^{13}C]BPO with MSB at 1.64×10^{-2} mol dm^{-3}. The two peaks near 166 ppm match those for a polymer of MMA made with [^{13}C]BPO but without additive[3]; the broad signal around 165.4 ppm must be attributed to benzoate groups adjacent to units derived from MSB. Comparison of spectral areas and application of equation (6) leads to a value of 496 for $k_{2,\text{MSB}}/k_{2,\text{MMA}}$; uncertainty of up to $\pm 10\%$ in the ratio of spectral areas would give the ratio of rate constants in the range 446–546. There is therefore reasonable overlap of the ranges obtained by the two approaches and $k_{2,\text{MSB}}/k_{2,\text{MMA}}$ can be taken as ~ 520; the corresponding quantities for STL and DPB, in place of MSB, are ~ 50 and 220, respectively, so that MSB is considerably more reactive towards the benzoyloxy radical than either STL or DPB.

The procedure involving determination of the ratio of benzoate to phenyl end groups, i.e. $x/(1-x)$, depends upon the assumption that any increase in the ratio, caused by the presence of an additive in the polymerizing MMA, results solely from the additive capturing benzoyloxy radicals to give benzoate end groups instead of phenyl end groups; it is possible however that two other effects could cause an increase in x. Phenyl radicals might abstract hydrogen atoms from the additive to give radicals which then form end groups not containing initiator fragments; if this process occurs, it could be detected by the fact that the total rate of incorporation of initiator fragments in polymer would be depressed by the presence of the additive. The experiments involving [^{14}C]BPO gave results showing that the 'loss' of phenyl groups from the polymer is of very little importance.

The second effect is connected with the assumption that k_1, the rate constant for the decarboxylation of the benzoyloxy radical, is unaffected by change in the composition of the reaction mixture. If the presence of an additive causes a reduction in k_1 and no allowance is made, the application of equation (4) inevitably leads to an overestimate of k_{2b}. It is most unlikely that k_1 is completely independent of the composition of the medium but the concentrations of MSB were low so that any influence on k_1 was probably very small.

The two effects referred to above cannot influence the value of k_{2b}/k_{2a} found by application of equations (5) and (6) because the competition between reactions (2a) and (2b) is studied directly.

The product of the addition of the benzoyloxy radical to MSB is believed to be the radical $\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}CH{\cdot}(C_6H_4{\cdot}CH_3){\cdot}\dot{C}H{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}CH_3}$ and it forms an end group corresponding to a STL-like structure. Such an end group is likely to be less reactive towards the benzoyloxy radical than the original MSB but appreciably more reactive than MMA. It should therefore be quite effective in capturing the initiating radical to give a unit represented as:



$$\mathrm{Ph.CO.O.}\underset{\mathrm{C_6H_4.CH_3}}{\underset{|}{\mathrm{CH}}}\mathrm{.}\overset{\mathrm{P_n}}{\overset{|}{\mathrm{CH}}}\mathrm{.C_6H_4.}\underset{\mathrm{P_m}}{\underset{|}{\mathrm{CH}}}\mathrm{.}\underset{\mathrm{C_6H_4.CH_3}}{\underset{|}{\mathrm{CH}}}\mathrm{.O.CO.Ph}$$

where P_n and P_m represent polymer chains formed independently at different stages in the polymerization. This feature will be studied further.

It appears that there have been no previous accounts of the involvement of MSB in radical polymerizations; it has however been the subject of quite extensive spectroscopic[5] and photophysical studies[6]. It has been used in liquid scintillation counting[7] but its emission is at wavelengths rather longer than those which are best for modern systems.

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