

# The reactivities of diarylbutadienes towards typical initiating radicals: the cases of the 1,4- and 2,3-isomers of diphenyl-1,3-butadiene

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Studies have been made of the reactivities of 1,4-diphenyl-1,3-butadiene and 2,3-diphenyl-1,3-butadiene towards the benzoyloxy, *p*-fluorobenzoyloxy and 1-cyano-1-methylethyl radicals. The 1,4-isomer has very high reactivity towards the aryloxy radicals but very low reactivity towards the substituted alkyl radical. The 2,3-isomer is moderately reactive towards all three initiating radicals. The results have been obtained by analyses for end-groups in samples of poly(methyl methacrylate) produced in the presence of one of the dienes with the appropriate source of initiating radicals.

(Keywords: diarylbutadienes; methyl methacrylate; radical copolymerization; end-groups; tracer studies;  $^{13}\text{C}$  n.m.r.)

## INTRODUCTION

The E-isomer of stilbene (STL) is very effective in capturing the benzoyloxy radical. At 60°C the rate constant for the process is about 50 times that for the reaction of the radical with methyl methacrylate (MMA) and about six times that for the corresponding reaction involving styrene. This reactivity of STL is retained and, in many cases, enhanced, if one or both of the phenyl groups is modified by substitution or is replaced by another aromatic group<sup>1</sup>. On the other hand, changing a phenyl group to a benzyl group leads to substantial reduction in reactivity towards the benzoyloxy radical<sup>2</sup>. It was concluded that very ready reaction with the benzoyloxy radical occurs only in those cases where the carbon atoms at both ends of the double bond are directly attached to aromatic groups. The reactivity is reduced quite markedly if the olefinic carbon atoms carry second substituents as in  $\alpha$ -methylstilbene and even more so in  $\alpha,\beta$ -dimethylstilbene<sup>3</sup>. This effect has been attributed to steric hindrance. In those cases in which it has been possible to compare the E and Z isomers of STL-like compounds, it has been found that the Z isomer is considerably the less reactive towards the benzoyloxy radical<sup>4</sup>.

The search for substances of other types possessing high reactivity towards the benzoyloxy radical has been extended to diarylbutadienes. This report refers to studies of 1,4- and 2,3-diphenyl-1,3-butadiene (1,4-DPB; 2,3-DPB). Two established approaches were used, both depending upon the use of benzoyl peroxide (BPO) to initiate polymerizations of MMA containing a diene. In one method of working, the peroxide was labelled with carbon-14 in its carbonyl groups and with tritium in the rings ( $^{14}\text{C}$ ,  $^3\text{H}$ -BPO) so that it was possible to determine for each of the polymers the ratio of the numbers of benzoate and phenyl end-groups<sup>3</sup>. The value of this ratio

depends upon the concentrations of MMA and the diene in the polymerizing system and upon the rate constants for their reactions with the benzoyloxy radical. In the second procedure, the peroxide was enriched with  $^{13}\text{C}$  at the carbonyl sites ( $^{13}\text{C}$ -BPO). The resulting polymers were examined by  $^{13}\text{C}$  n.m.r. so that the number of benzoate end-groups attached to MMA units could be compared with the number joined to units derived from the diene. Supplementary evidence was obtained from experiments in which MMA containing a diene was polymerized using *p*-fluorobenzoyl peroxide (FBPO) as initiator. The *p*-fluorobenzoate end-groups in the polymers were studied by  $^{19}\text{F}$  n.m.r.<sup>5</sup>.

In spite of being very reactive towards the benzoyloxy radical, the STL-like compounds are relatively unreactive towards the 1-cyano-1-methylethyl radical. The effect is attributed, in part at least, to serious steric hindrance to the attachment of the carbon-centred radical to an olefinic carbon atom also bearing a substituent. 1,4-DPB and 2,3-DPB have been examined for reactivity towards the 1-cyano-1-methylethyl radical. For this purpose,  $^{13}\text{C}$ -enriched azobisisobutyronitrile ( $^{13}\text{C}$ -AIBN) was used to initiate polymerizations of MMA containing a diene and then  $^{13}\text{C}$  n.m.r. was used to compare the numbers of initiator fragments attached to the two types of units in the polymers<sup>6</sup>.

## EXPERIMENTAL

Most of the materials and experimental procedures have been previously specified<sup>1-6</sup>. 1,4-DPB (Aldrich) was recrystallized from a toluene/methanol mixture. A computer simulation, using data derived from butadiene, afforded calculated spectra for olefinic resonances in 1,4-DPB similar in form to a 400 MHz  $^1\text{H}$  n.m.r. spectrum and wholly consistent with *trans-trans* geometry. Polymerizations were performed at 60°C under air-free conditions using toluene as diluent; conversions did not

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exceed 8%. Polymers were recovered by precipitation in methanol and purified by reprecipitations.

## RESULTS

Polymerizations of MMA were initiated by  $^{14}\text{C}$ ,  $^3\text{H}$ -BPO for which  $(^3\text{H activity})/(^{14}\text{C activity})$  was 1.35. For polymers 1 and 2, the initial values of  $[\text{MMA}]$  in the polymerizing system were 3.15 and 2.36 mol dm $^{-3}$ , respectively and those of  $10^2 \times [1,4\text{-DPB}]$  were 5.35 and 3.75 mol dm $^{-3}$ . The values of  $(^3\text{H activity})/(^{14}\text{C activity})$  for the polymers were 1.67 and 1.74. For polymer 3, the initial values of  $[\text{MMA}]$  and  $10^2 \times [2,3\text{-DPB}]$  during the polymerization were 3.15 and 15.80 mol dm $^{-3}$  and  $(^3\text{H activity})/(^{14}\text{C activity})$  was 2.17.

Use is made of the relationships

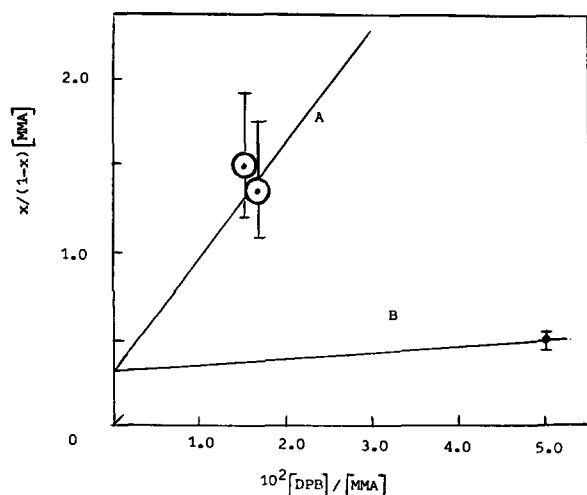
$$\frac{\text{number of benzoate end-groups}}{\text{sum of numbers of benzoate and phenyl end-groups}} = x = \frac{^{14}\text{C activity of polymer}}{^{14}\text{C activity of peroxide}} \times \frac{^3\text{H activity of peroxide}}{^3\text{H activity of polymer}} \quad (1)$$

and

$$x/(1-x)[\text{MMA}] = k_2/k_1 + k'_2[1,4\text{-DPB}]/k_1[\text{MMA}] \quad (2)$$

where  $k_1$  is the rate constant for decarboxylation of the benzoyloxy radical and  $k_2$  and  $k'_2$  are the rate constants for attachment of the radical to MMA and 1,4-DPB, respectively. In a relationship corresponding to equation (2) but involving 2,3-DPB instead of 1,4-DPB,  $k''_2$  refers to the attachment of the benzoyloxy radical to 2,3-DPB. It is known that  $k_2/k_1$  is 0.31 dm $^3$  mol $^{-1}$  and the lines drawn in *Figure 1* lead to values of 65 and 4 dm $^3$  mol $^{-1}$  for  $k'_2/k_1$  and  $k''_2/k_1$ , respectively, giving 210 for  $k'_2/k_2$  and 13 for  $k''_2/k_2$ . Error bars shown with the points in *Figure 1* correspond to 5% uncertainties in the values of  $x$ , as found from four measurements of radioactivity.

*Figure 2* shows parts of the 100 MHz  $^{13}\text{C}$  n.m.r. spectra of samples of polyMMA prepared using  $^{13}\text{C}$ -BPO. In experiments 4 and 5,  $10^2 \times [1,4\text{-DPB}]/[\text{MMA}]$  had values of 0.92 and 1.70 respectively; in experiments 6 and 7, the values of  $10^2 \times [2,3\text{-DPB}]/[\text{MMA}]$  were 2.47 and 4.93. In experiment 8, MMA was used without additive.



**Figure 1** Plots showing the effects of 1,4-diphenylbutadiene (curve A) and 2,3-diphenylbutadiene (curve B) on the balance between benzoate and phenyl end-groups in poly(methyl methacrylate) prepared using benzoyl peroxide as initiator

at *c.* 166 and 165.6 ppm arise from enriched benzoate groups attached to MMA units. For polymers 4 and 5, they are accompanied by upfield signals between *c.* 164.5 and 165.5 ppm, more pronounced for the polymer made from the system richer in 1,4-DPB. These additional signals are attributable to enriched initiator fragments joined to units derived from 1,4-DPB. The precise nature of these units need not be considered at this stage. The ratio of the area covered by the peaks around 165 ppm to that covered by the peaks near 166 ppm is approximately 2.8 for polymer 4 and 4.4 for polymer 5. Use of the relationship

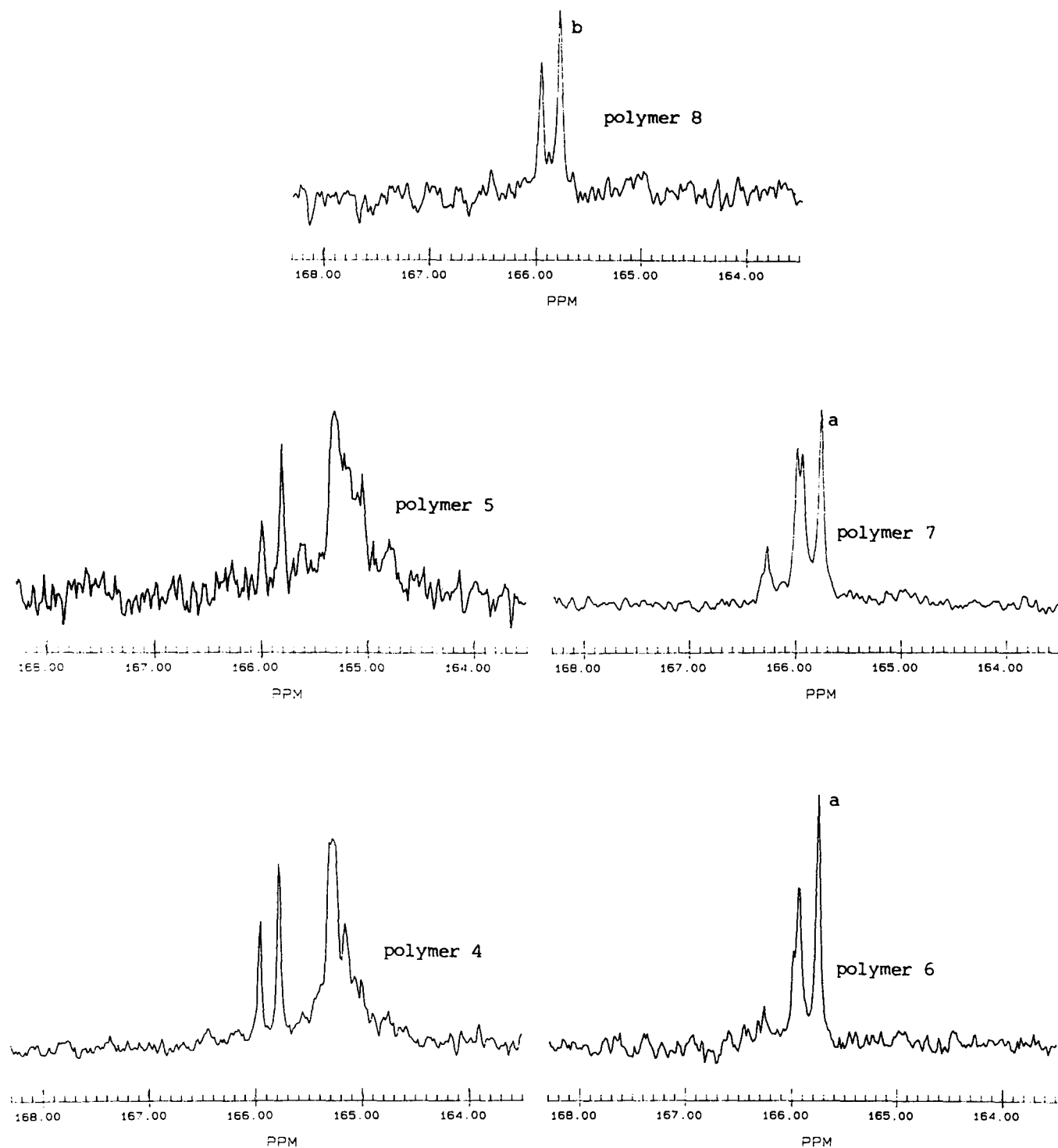
$$\frac{\text{area for benzoate end-groups adjacent to 1,4-DPB units}}{\text{area for benzoate end-groups adjacent to MMA units}} = \frac{k'_2[1,4\text{-DPB}]}{k_2[\text{MMA}]} \quad (3)$$

gives values of 300 and 260 for  $k'_2/k_2$ .

The evident differences between the spectrum of polymer 8 and those of polymers 6 and 7 shown in *Figure 2* indicate that some of the benzoate end-groups in the latter polymers are adjacent to units derived from 2,3-DPB. The complexity of the spectra makes interpretation difficult but it can be noted that peak a for polymers 6 and 7 seems to be resolved and to match peak b for polymer 8, prepared in the absence of 2,3-DPB. Peak a covers areas which are 43% and 35% of the total areas for benzoate end-groups in polymers 6 and 7, respectively. The area for peak b is 56% of the total area for the end-groups for polymer 8. The total contributions of benzoate groups attached to MMA units in polymers 6 and 7 are therefore estimated as  $(43 \times 100/56)\%$ , i.e. 77%, and  $(35 \times 100/56)\%$ , i.e. 62.5%, respectively. Application of an equation similar to equation (3) then leads to values of about 12 and 15 for  $k''_2/k_2$ .

Polymers 9–12 were made from MMA using FBPO as initiator. For polymers 9 and 10,  $10^2 \times [1,4\text{-DPB}]/[\text{MMA}]$  had values of 0.56 and 1.13 respectively;  $10^2 \times [2,3\text{-DPB}]/[\text{MMA}]$  was 1.71 for polymer 11 and no additive was present during the preparation of polymer 12. Comparisons of the 93.7 MHz  $^{19}\text{F}$  n.m.r. spectra in *Figure 3* show that many of the *p*-fluorobenzoate end-groups in polymers 9 and 10 are attached to units derived from 1,4-DPB. Polymer 11 evidently contains some *p*-fluorobenzoate groups joined to units formed from 2,3-DPB, giving signals in the range 7.0–7.4 ppm. Integration of the spectrum and application of an equation similar to equation (3) indicates that the rate constant for reaction of the *p*-fluorobenzoyloxy radical with 2,3-DPB is approximately 20 times that for the reaction with MMA. Measurements on a difference spectrum for polymers 10 and 12 indicate a value in the region of 100 for the ratio of the rate constants for the additions of the *p*-fluorobenzoyloxy radical to 1,4-DPB and MMA.

*Figure 4* shows part of the 25 MHz  $^{13}\text{C}$  n.m.r. spectrum of polymer 13 made from MMA using  $^{13}\text{C}$ -AIBN in a system in which  $[2,3\text{-DPB}]/[\text{MMA}]$  was 0.15. The signals arise from the enriched methyl carbon atoms in  $(\text{CH}_3)_2\text{C}(\text{CN})$  end-groups. The relative areas covered by the peaks centred at *c.* 25.4, 27.5 and 30.0 are 1.0, 0.4 and 1.4, respectively. The peak at 25.4 ppm is attributed to initiator fragments attached to MMA units and that at 27.5 ppm to fragments joined to units derived from 2,3-DPB. The other signals of the pairs for the two types



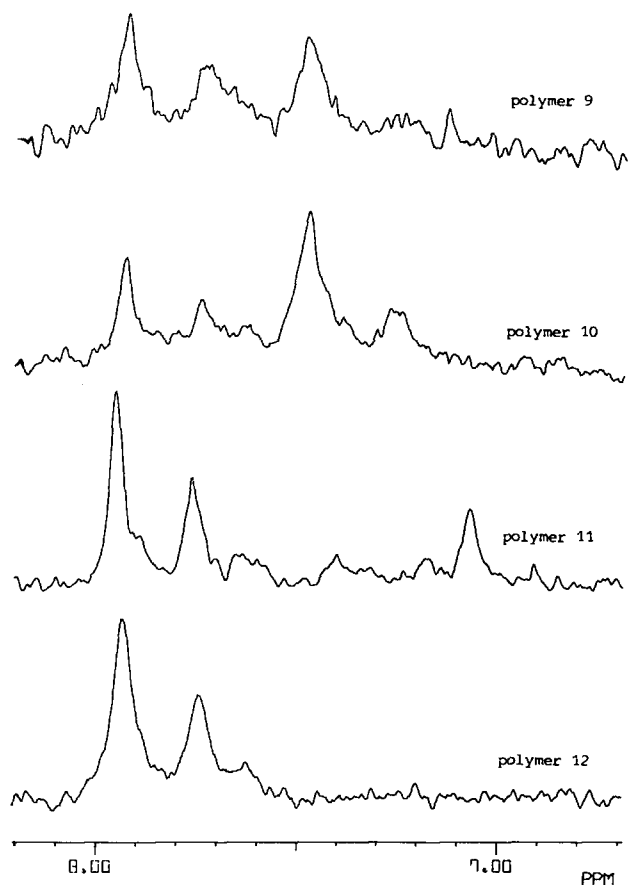
**Figure 2** Parts of the 100 MHz  $^{13}\text{C}$  n.m.r. spectra of samples of poly(methyl methacrylate) prepared using  $^{13}\text{C}$ -benzoyl peroxide as initiator. Polymer 4,  $10^2 \times [1,4\text{-DPB}]/[\text{MMA}] = 0.92$ ; polymer 5,  $10^2 \times [1,4\text{-DPB}]/[\text{MMA}] = 1.70$ ; polymer 6,  $10^2 \times [2,3\text{-DPB}]/[\text{MMA}] = 2.47$ ; polymer 7,  $10^2 \times [2,3\text{-DPB}]/[\text{MMA}] = 4.93$ ; polymer 8, MMA without additive

of initiator fragments must together form the peak at *c.* 30.0 ppm, covering an area equal to the sum of the areas covered by the other peaks. The rate constants for the reactions leading to attachments of the 1-cyano-1-methylethyl radical to MMA and 2,3-DPB are taken as  $k_3$  and  $k_3''$  respectively. Application of an equation similar to equation (3) gives a value of 2.7 for  $k_3''/k_3$ . Polymers were also made from systems containing 1,4-DPB and  $^{13}\text{C}$ -AIBN. They showed the pair of  $^{13}\text{C}$  n.m.r. signals corresponding to  $(\text{CH}_3)_2\text{C}(\text{CN})\cdot\text{MMA}$  end-groups but, even for the case where  $[1,4\text{-DPB}]/[\text{MMA}]$  was as large

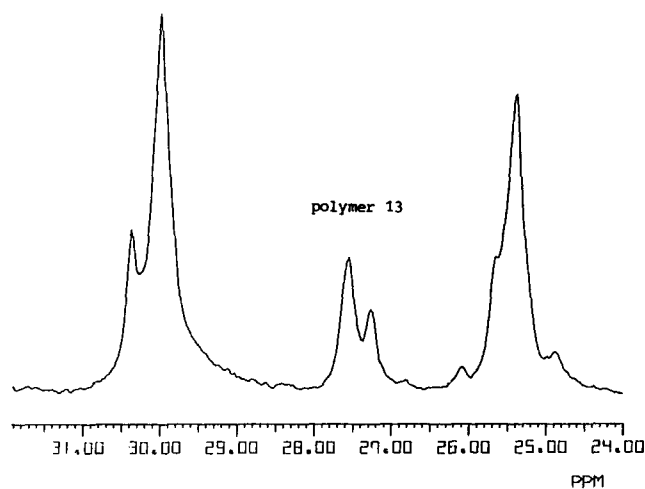
as 0.18, the only indication of the presence of initiator fragments attached to units derived from 1,4-DPB was slight imbalance between the signals centred at *c.* 25.4 and 30.0 ppm. It must be concluded that 1,4-DPB is very much less reactive than 2,3-DPB towards the 1-cyano-1-methylethyl radical.

#### DISCUSSION

The procedure involving  $^{14}\text{C}$ ,  $^3\text{H}$ -BPO and that depending upon  $^{13}\text{C}$ -BPO give similar results for the reactivities at



**Figure 3**  $^{19}\text{F}$  n.m.r. spectra (93.7 MHz) of samples of poly(methyl methacrylate) prepared using *p*-fluorobenzoyl peroxide as initiator. Polymer 9,  $10^2 \times [1,4\text{-DPB}]/[\text{MMA}] = 0.56$ ; polymer 10,  $10^2 \times [1,4\text{-DPB}]/[\text{MMA}] = 1.13$ ; polymer 11,  $10^2 \times [2,3\text{-DPB}]/[\text{MMA}] = 1.71$ ; polymer 12, MMA without additive



**Figure 4** Part of the 25 MHz  $^{13}\text{C}$  n.m.r. spectrum of poly(methyl methacrylate) obtained from a system in which  $[2,3\text{-DPB}]/[\text{MMA}]$  was 0.15 and  $^{13}\text{C}$ -azobisisobutyronitrile was used as initiator

$60^\circ\text{C}$  of 1,4- and 2,3-DPB towards the benzoyloxy radical although the agreement is not good. The errors in both procedures are by no means small. It is clear that the 2,3-isomer quite readily captures the benzoyloxy radical and the rate constant for the reaction is about 15 times that for the case of MMA. The 1,4-isomer is however more than 200 times as reactive as MMA towards the benzoyloxy radical. In this connection therefore, 1,4-DPB resembles the more reactive of the STL-like com-

pounds. The results with FBPO provide confirmation of the substantial difference between the reactivities of 1,4- and 2,3-DPB towards aryloxy radicals.

The reaction between the benzoyloxy radical and 1,4-DPB most probably leads to end-groups  $\text{Ph}\cdot\text{CO}\cdot\text{O}\cdot\text{CHPh}\cdot\text{CH}(\text{CH}\cdot\text{CHPh})-$  and  $\text{Ph}\cdot\text{CO}\cdot\text{O}\cdot\text{CHPh}\cdot\text{CH}:\text{CH}\cdot\text{CHPh}-$  but it is not yet possible to make deductions about their relative numbers. There is a resemblance between the reactions of the benzoyloxy radical with STL and 1,4-DPB. In both cases, the radical becomes attached to an olefinic carbon atom carrying a phenyl group. Further, the carbon atom at the other end of the double bond in both STL and 1,4-DPB is joined to a conjugated system which is either a phenyl or a styryl group.

Reaction between the benzoyloxy radical and 2,3-DPB is likely to lead to end-groups  $\text{Ph}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CPh}(\text{CPh}:\text{CH}_2)-$  and  $\text{Ph}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CPh}:\text{CPh}\cdot\text{CH}_2-$ . The former seems the more likely. In this case, the radical interacts with the methylene group so that the reaction resembles that with a monomer such as styrene rather than that with STL and so its rate constant is not particularly large.

Although 2,3-DPB is much less reactive than the 1,4-compound towards the benzoyloxy and *p*-fluorobenzoyloxy radicals, it is considerably the more reactive isomer with respect to the 1-cyano-1-methylethyl radical. Attack of the  $(\text{CH}_3)_2\dot{\text{C}}(\text{CN})$  radical on 2,3-DPB most probably occurs at a methylene group and so the reaction is expected to have characteristics generally similar to those for reactions of the radical with monomers of the types  $\text{CH}_2:\text{CHX}$  and  $\text{CH}_2:\text{CXY}$ . In fact, 2,3-DPB is 2.5 times as reactive as MMA but it must be noted that the diene has two sites of equal reactivity in its molecule whereas the other monomer effectively has only one point of attack. Any reaction of  $(\text{CH}_3)_2\dot{\text{C}}(\text{CN})$  with 1,4-DPB would be expected to occur at a carbon atom bearing a phenyl group and to be of little importance. This view is based on the low reactivity of STL-compounds towards this radical and also on the fact that head-addition of the radical to monomers  $\text{CH}_2:\text{CHX}$  and  $\text{CH}_2:\text{CXY}$  is rare.

The ready reaction between 2,3-DPB and the carbon-centred 1-cyano-1-methylethyl radical suggests that the diene would engage quite readily in radical copolymerizations. This belief is confirmed for MMA (monomer-1) as comonomer. Values of 0.71 and 0.13 for the reactivity ratios  $r_1$  and  $r_2$ , respectively<sup>7</sup> indicate that 2,3-DPB is more reactive than MMA towards the polyMMA radical and also that reaction between monomeric 2,3-DPB and a radical ending with a 2,3-DPB unit is by no means negligible.

There are few reports on polymerizations of 1,4-DPB. It has been used<sup>8</sup> as an additive in the polymerization of butadiene with organobarium initiators and there is evidence for its incorporation in the polymer. Formation of a homopolymer of 1,4-DPB using other anionic initiators has been described<sup>9</sup> but no mention has been found of its participation in radical polymerizations.

Low levels of incorporation of STL in polymers of various monomers have been measured using  $^{14}\text{C}$ -STL<sup>10</sup> but it has not yet been possible to apply a similar procedure for 1,4-DPB. High field  $^{13}\text{C}$  n.m.r. spectra of polymers of MMA made in the presence of either 1,4- or 2,3-DPB have been examined for evidence for incorporation of aromatic groups. Polymers 6 and 7, prepared

using 2,3-DPB, gave rise to structured signals around 128 ppm so that aromatic groups were clearly present in the polymers. According to the monomer reactivity ratios already quoted, the polymers contained approximately 29 and 15 MMA units respectively for each 2,3-DPB unit. For polymers 4 and 5, prepared in the presence of 1,4-DPB, there was evidence for the incorporation of only very few 1,4-DPB units at any sites other than those adjacent to benzoate end-groups. This result is expected because incorporation of the diene would require it to react with a carbon-centred radical, namely the polyMMA radical, but it has been shown that 1,4-DPB is almost inert towards the carbon-centred initiating radical  $(\text{CH}_3)_2\dot{\text{C}}(\text{CN})$ .

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