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Reactivities towards the benzoyloxy radical of some acetylenic compounds when used in the polymerization of methyl methacrylate

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Summary

Phenylacetylene, diphenylacetylene and 1,4-diphenylbutadiyne are at 60°C appreciably less effective in capturing the benzoyloxy radical than their olefinic counterparts i.e. styrene, stilbene and 1,4-diphenylbuta-1,3-diene respectively.

Introduction

Stilbene and related substances (1) and also 1,4-diarylbutadienes (2) are very effective in capturing the benzoyloxy radical; in some cases, the rate constants at 60°C for the reactions with the radical exceed those for the corresponding processes involving methyl methacrylate (MMA) and styrene (STY) by factors approaching 600 and 75 respectively. The search for substances of other types showing similar high reactivities towards the benzoyloxy radical has included examination of some acetylenic compounds containing phenyl groups, viz. phenylacetylene (PA), diphenylacetylene (DPA) and 1,4-diphenylbutadiyne (DPB), regarded as related to STY, stilbene and 1,4-diphenylbuta-1,3-diene respectively.

Acetylenic compounds generally are not regarded as possible comonomers to be used in radical polymerizations of MMA for example; there is however evidence that radicals are involved in the thermal polymerization of PA (3) and in its alternating copolymerization with sulphur dioxide (4). It seemed possible that certain acetylenic compounds might resemble stilbene and 1,4-diphenylbutadiene in the sense that they might react readily with the oxygen centred benzoyloxy radical and so to show a great tendency to become incorporated at sites adjacent to benzoate end-groups of macromolecules. If this effect were displayed, the resulting polymers would contain carbon-carbon double bonds (derived from the triple bonds of the acetylenic compound) in the main chains at positions very close to the chain-ends; the double bonds might be useful as centres for subsequent chemical reaction (5).

The reactivities of PA, DPA and DPB have been examined by two established procedures, both involving analyses for end-groups in polyMMA prepared using benzoyl peroxide (BPO) as initiator in the presence of the acetylenic compound. One procedure relies upon the use of BPO labelled with carbon-14 in the carbonyl groups and with tritium in the rings (6); the reactivity of the additive towards the benzoyloxy radical is assessed from its effect upon the balance between the numbers of benzoate and phenyl end-groups derived from the initiator. The other procedure requires the use of BPO enriched with carbon-13 at its carbonyl sites (1). The isotopic enrichment increases the sensitivity for detection by ^{13}C-NMR of benzoate end-groups and it is possible to compare the number of benzoate groups adjacent to MMA units with the number joined to units derived from the additive; the rate constants for the reactions of MMA and additive with the benzoyloxy radical can then be compared.

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Experimental

The preparations of the various types of BPO have been referred to already (1,6). Commercial samples of PA, DPA and DPB were purified, the first-named by distillation in nitrogen and the others by recrystallization. Polymerizations were performed in air-free solutions in toluene at 60°C; they were monitored by dilatometry and were carried to conversions not exceeding 10%. Polymers were recovered by precipitation in methanol and purified by two reprecipitations. Measurements of radioactivity by liquid scintillation counting (6) and recording of NMR spectra (1) have been described. The assays were spread over a period of 12 months and were corrected for decay of tritium taking the half-life of that isotope as 12 years.

Results and Discussion

The effects of PA, DPA and DPB at concentrations up to 0.20 mol dm^{-3} upon the rates of polymerization of MMA were examined for systems in which the concentrations of monomer and BPO were 3.10 and 0.83×10^{-2} mol dm^{-3} respectively. DPA did not affect the rate; with DPB or PA at 0.20 mol dm^{-3}, the rates were 70% and 35% respectively of that in the absence of additive.

A fraction $\underline{x}$, defined as (no. of benzoate end-groups)/(sum of nos. of benzoate and phenyl end-groups) was found for each polymer prepared using doubly-labelled peroxide (see Table 1) using the expression (6)

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

Table 1. Experiments involving doubly-labelled benzoyl peroxide

additive (mol dm^{-3})	MMA (mol dm^{-3})	(^{3}H-activity)/ ^{14}C-activity) for polymer	fraction $\underline{x}$
PA; 0.272	2.36	2.95	0.458
DPA; 0.155	3.10	2.40	0.562
DPB; 0.044	3.10	2.70	0.500

for peroxide, (^{3}H-activity)/(^{14}C-activity) = 1.35

The rate constants for decarboxylation of the benzoyloxy radical, its addition to MMA and its addition to the additive are taken as k_1, k_2 and k_2' respectively. The equation

$$\frac{\underline{x}}{(1 - \underline{x})} = \frac{k_2\,[\text{MMA}]}{k_1} + \frac{k_2'[\text{additive}]}{k_1} \qquad \text{(I)}$$

is then used; k_2/k_1 is taken as 0.31 mol^{-1} dm^3 and k_2'/k_1 is found. Application of equation (I) to the results in Table 1 leads to values of 0.4, 2.1 and 0.9 mol^{-1} dm^3 for PA, DPA and DPB respectively;these values are very sensitive to uncertainties in $\underline{x}$ and changes of ± 5% in that quantity lead to values of k_2'/k_1 in the ranges 0.1-0.7, 1.2-3.1 and 0-3.3 mol^{-1} dm^3 for PA, DPA and DPB respectively; in the case of DPB, use of $\underline{x} = 0.475$ leads to a negative value for k_2'/k_1.

The quantities corresponding to k_2'/k_1 for STY, stilbene and 1,4-diphenylbutadiene are 2.5, 13 and 75 mol^{-1} dm^3 respectively. Evidently PA, DPA and DPB are noticeably less reactive at 60°C than their olefinic counterparts.

Figure 1 shows part of the 100 MHz ^{13}C-NMR spectrum of a polymer of MMA made from a system in which [MMA] and [DPA] were 3.25 and 0.27 mol dm^{-3} respectively and ^{13}C-BPO was used as initiator. The carbonyl carbons in PhCO.O-

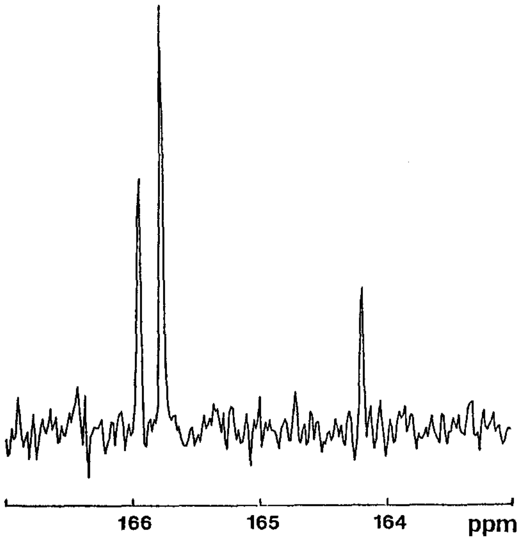

Figure 1. Part of the 100 MHz ^{13}C-NMR spectrum of a polymer of methyl methacrylate (MMA) prepared at 60^{o}C in toluene solution using ^{13}C-BPO in the presence of diphenylacetylene (DPA). The concentrations of MMA and DPA are given in the text.

groups adjacent to MMA units give rise to a characteristic pair of peaks near 166 ppm (1); the signal at 164.2 ppm must be associated with benzoate groups joined to units derived from DPA. The ratio of the areas covered by the peaks corresponding to the two types of benzoate groups is 0.15:1. The rate constants k_2 and k_2' can be compared by means of the relationship

$$\frac{\text{spectral area for Ph}\dot{\text{C}}\text{O.O.MMA-}}{\text{spectral area for Ph}\dot{\text{C}}\text{O.O.DPA-}} = \frac{k_2[\text{MMA}]}{k_2'[\text{DPA}]}$$

and a value of 1.8 is found for k_2'/k_2, corresponding to k_2'/k_1 being 0.6 $\text{mol}^{-1}\ \text{dm}^3$ i.e. somewhat outside the range of values from the experiment in which radioactive BPO was used but confirming that DPA has a reactivity towards the benzoyloxy radical considerably less than that of stilbene.

The discrepancy between the results obtained using the two types of BPO is caused in part at least by uncertainties in experimental results; it must be noted also that the procedure involving comparison of the numbers of benzoate and phenyl end-groups in a polymer depends upon the assumption that the rate constant for the decarboxylation of the benzoyloxy radical is not affected by the presence of additive. If an interaction between DPA and the benzoyloxy radical could reduce the tendency for decarboxylation of the radical (i.e. reduce k_1) without permanent attachment of the radical to DPA, then the procedure involving application of equation (I) would lead to overestimate of k_2'.

The ^{13}C-NMR spectrum of a polymer prepared from MMA at 3.05 mol dm^{-3}, using ^{13}C-BPO and DPB at 0.10 mol dm^{-3}, showed the signals expected for PhCO.O.MMA- end-groups and small additional signals near 165 ppm attributed to PhCO.O.DPB- end-groups. Exact measurements were not possible but it was clearly confirmed that DPB is much less efficient than 1,4-diphenylbutadiene in capturing the benzoyloxy radical. A polymer similarly prepared but using PA as additive gave overlapping NMR signals and measurements could not be made although it was apparent that the number of PhCO.O.PA- end-groups was not large.

El Soueni, Tedder and Walton (7) studied the additions in the gas phase of the trifluoromethyl radical to some acetylenic compounds. The radicals were generated by the photolysis of trifluoromethyl iodide so that the reactions could be examined over a wide range of temperatures and reliable values of the Arrhenius parameters, A and E, could be obtained. Both parameters are larger for the reactions involving alkynes than those for the additions to the alkenes; the rates for the two types of process become approximately equal at comparatively high temperatures, say 150°C. Similar conclusions were reached in an earlier study which included PA (8). It has been reported that substituents have similar effects on the reactivities towards radicals of alkenes and alkynes (7). It has also been concluded (9) that, for addition of the methyl radical, both the A and E parameters are higher for acetylene than for ethylene. It is improbable that the general pattern of behaviour for reactions in the gas phase would differ from that for similar processes in liquids.

Bamford (10) has used data for gas phase additions of small radicals such as trifluoromethyl to olefins to consider the reactivities of radicals in polymerization processes in the liquid phase and to explain factors influencing rate and regiospecificity in addition reactions. The reactions of the trifluoromethyl and benzoyloxy radicals can usefully be compared since both radicals are electrophilic in character. It seems reasonable that PA, DPA and DPB should be comparatively unreactive towards the benzoyloxy radical at 60°C. It would be useful to have information on the reactivities over a wide range of temperatures but BPO can properly be used as a thermal initiator of polymerization only between say 50° and 85°C. It can be used as a photo-initiator at lower temperatures but such conditions would appear not to favour the reaction of the benzoyloxy radical with the acetylenic compounds. The benzoyloxy radical can be produced at suitable rates at temperatures up to say 115°C by dissociation of esters of perbenzoic acid e.g. tert.butyl perbenzoate. If the perester is used to initiate polymerization, it is expected that 50% of the initiation steps involve tert.butoxy or derived methyl radicals; further, the decarboxylation of the benzoyloxy radical is likely to occur more readily at elevated temperatures. These considerations indicate that it is impracticable to use a mixture of a monomer, such as MMA, and an acetylenic compound, such as PA, DPA or DPB, to prepare polymers containing a high proportion of end-groups consisting of a benzoate group attached to an unsaturated unit derived from the acetylenic compound.

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