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Effects of some unsaturated carbonyl compounds upon the formation of end-groups during the polymerization of methyl methacrylate initiated by benzoyl peroxide

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Summary

Several unsaturated carbonyl compounds, derived from the condensation of methyl ketones with aromatic aldehydes, have been used as additives for polymerizations of methyl methacrylate initiated by benzoyl peroxide at 60°. They increase the ratio of benzoate to phenyl end-groups derived from the peroxide; the effects are quite marked for cinnamalacetophenone and dicinnamalacetone and they indicate efficient capture of the benzoyloxy radical by the additives. It is shown also that dibenzoylethylene is unreactive towards the benzoyloxy radical.

Introduction

The E-isomers of stilbene (1) and various related substances, e.g. 2-styrylnaphthalene (2), are very effective in capturing the benzoyloxy radical although they are unreactive towards carbon-centred radicals. The relative values of the rate constants at 60°C for the reactions of the benzoyloxy radical with methyl methacrylate (MMA), styrene (STY), stilbene and 2-styryl naphthalene are 1, 8, 50 and 117 respectively. Rapid reaction with the benzoyloxy radical has been found also for the trans-trans isomers of those 1,4-diarylbuta-1,3-dienes which have been examined (3,4); thus the rate constant for the attachment of the benzoyloxy radical to 1,4-diphenylbutadiene at 60° is about 200 times that for the corresponding reaction for MMA. It appears that high reactivity towards the benzoyloxy radical is displayed if an unsaturated substance has a structure in which there is an aromatic group joined to the carbon atom to which the radical becomes attached and if there is extensive conjugation through the molecule. In those cases where both the E- and Z-isomers of stilbene-like compounds have been studied, it has been found that the former are much more reactive than the latter.

In a search for substances of other types having high reactivity towards the benzoyloxy radical, an examination has been made of unsaturated compounds containing carbonyl groups as well as aromatic groups, viz. benzalacetone (Ph.CH:CH.CO.Me), chalcone (Ph.CH:CH.CO.Ph), cinnamalacetophenone (Ph.CH:CH.CH:CH.CO.Ph), dibenzalacetone (Ph.CH:CH.CO.CH:CH.Ph), dicinnamalacetone (Ph.CH:CH.CH:CH.CO.CH:CH.CH:CH.Ph) and dibenzoylethylene (Ph.CO.CH:CH.CO.Ph).

Procedures for assessing the reactivity towards the benzoyloxy radical of a substance involve its use as an additive during the polymerization of a monomer such as MMA with benzoyl peroxide (BPO) as the source of the initiating radicals; the resulting polymer is then analyzed for end-groups derived from the peroxide. The method applied in the present case depends upon the use of BPO labelled in its rings with tritium and in its carbonyl groups with carbon-14 (5). Comparison of the ^{14}C- and ^{3}H-contents of a polymer with those of the original peroxide makes it possible to compare the numbers of benzoate and phenyl end-groups in the polymer and to find the values of

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k_2/k_1 and k_2'/k_1 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 the attachment of the benzoyloxy radical to MMA and the additive respectively; essentially, a study is made of the extent to which the additive suppresses the decarboxylation by capturing the benzoyloxy radical.

Experimental

The six carbonyl compounds under consideration were purified by recrystallizations. Polymerizations were performed at 60°C with MMA at 3.00 mol dm^{-3} and BPO at 0.80×10^{-2} mol dm^{-3} in toluene under air-free conditions; they were monitored by dilatometry and conversions did not exceed 10%. The polymers were recovered by precipitation in methanol and purified by two further precipitations. Measurements of specific activities in Bq g^{-1} were made by scintillation counting of solutions in toluene using an LKB 'Spectral' Liquid Scintillation Counter (5).

Results and Discussion

The polymerization of MMA initiated by BPO under the specified conditions was slightly retarded by benzalacetone, chalcone and dibenzalacetone; each of these additives at 0.30 mol dm^{-3} reduced the rate to about 80% of the value in its absence. Cinnamalacetophenone and dicinnamalacetone were much more effective retarders; the rate of polymerization was halved with the acetophenone derivative at about 3×10^{-2} mol dm^{-3} or with the acetone derivative at about 0.3×10^{-2} mol dm^{-3}. Dibenzoylethylene at concentrations up to at least 0.20 mol dm^{-3} hardly affected the rate of polymerization.

Polymerizations initiated by doubly-labelled BPO are referred to in Table 1. For each polymer, a fraction *x* defined as (no. of benzoate end-groups)/(sum of nos. of benzoate and phenyl end-groups) is given by

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

The relationship

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

is used to compare the rate constants (k_2') for the reactions of the added substances with the benzoyloxy radical, using the decarboxylation of the radical as a reference reaction (5).

Table 1. Polymerizations of methyl methacrylate containing various additives, initiated by doubly-labelled benzoyl peroxide.

additive	[additive]/[MMA]	(^{3}H-activity)/(^{14}C-activity) for polymer	fraction *x*
benzalacetone	0.073	2.25	0.573
"	0.110	2.18	0.592
"	0.147	2.09	0.617
chalcone	0.070	2.41	0.535
"	0.213	2.09	0.617
cinnamalacetophenone	1.09×10^{-2}	2.40	0.538
"	1.73×10^{-2}	2.30	0.561
dibenzalacetone	0.067	2.24	0.576
"	0.110	2.13	0.606
dicinnamalacetone	0.21×10^{-2}	2.53	0.510
"	0.24×10^{-2}	2.52	0.512
dibenzoylethylene	0.033	2.70	0.478
"	0.060	2.62	0.492

for each polymerization, [MMA] = 3.00 mol dm^{-3}
(^{3}H-activity)/(^{14}C-activity) for polymer = 1.29

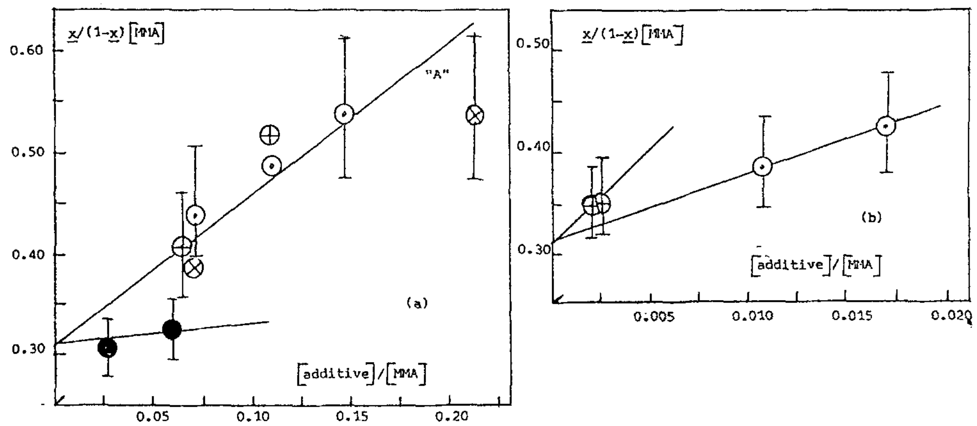

Figure 1. Presentation of data on the relative numbers of benzoate and phenyl end-groups, derived from benzoyl peroxide, in polymers of methyl methacrylate prepared at 60°C in the presence of additives at various concentrations. (a) ● dibenzoylethylene; ⊙ benzalacetone; ⊗ chalcone; ⊕ dibenzalacetone. (b) ⊙ cinnamalacetophenone; ⊕ dicinnamalacetone.

Figure 1 shows plots of x/(1-x)[MMA] vs. [additive]/[MMA]. It is known that k_2/k_1 is 0.31 mol^{-1} dm^3, so fixing the intercept on the ordinate for each of the lines; the quantity corresponding to k_2/k_1 in the case of STY is 2.50 mol^{-1} dm^3 (6). The quantity x/(1-x) is very sensitive to small changes in x and the effects of uncertainties of ±5% are indicated for some of the points in Figure 1. The line "A" drawn in Figure 1a corresponds to a value of 1.5 mol^{-1} dm^3 for k_2'/k_1; it is clear that benzalacetone, chalcone and dibenzalacetone can hardly be distinguished in respect of their reactivities towards the benzoyloxy radical and that for each of them k_2'/k_1 can probably be taken as 1.5 ± 0.3 $mol^{-1}dm^3$. Dibenzoylethylene has low reactivity for the radical and k_2'/k_1 can be taken as 0.2 ± 0.2 $mol^{-1}dm^3$. Cinnamalacetophenone and dicinnamalacetone are quite reactive towards the benzoyloxy radical and the values of k_2'/k_1 appear to be 6.5 ± 1.5 and 18 ± 4 mol^{-1} dm^3 respec.

It is evident that, for the reactions of the six substances with the benzoyloxy radical, only cinnamalacetophenone and dicinnamalacetone show reactivities which can be described as high and comparable with that of stilbene; the rate constants for the reactions of these derivatives of cinnamaldehyde are respectively about 21 and 58 times that for the corresponding reaction involving MMA and 2.6 and 7.2 times that for the reaction with STY. The low reactivity of dibenzoylethylene is consistent with the fact that its structure does not satisfy one of the suggested criteria for high reactivity towards the benzoyloxy radical viz. that an aromatic group should be directly attached to an olefinic carbon atom; this condition is satisfied for the other five substances. Benzalacetone, chalcone and dibenzalacetone possess moderate reactivities, intermediate between those of MMA and STY; it must be supposed that, in these carbonyl compounds, the conjugation is not extensive enough for high reactivity to be displayed. The higher reactivities of cinnamalacetophenone and dicinnamalacetone can be attributed to the greater conjugation in their molecules.

Benzalacetone and chalcone can be regarded as quite simple beta-substituted derivatives of STY. It has been pointed out (7,8) that the benzoyloxy radical is strongly electrophilic in character and that introduction of a substituent at either the alpha- or beta-position in STY modifies the reactivity towards the radical according to the electron-withdrawing or -repelling character of the substituent. Thus the presence of the electron-repelling methyl group at either the alpha- or beta-position in STY causes the reactivity towards the radical to be about twice that of STY itself (7). Both benzalacetone and chalcone contain an electron-withdrawing group (-CO.Me or -CO.Ph) which can be expected to make the reactivity less than that of STY, as actually found; the substituents may also reduce the reactivity as a result of steric effects.

The use of radioactively-labelled BPO can give no direct indication of the mode of attachment of the benzoyloxy radical to the molecule of an unsaturated substance. This important information can, in principle at least, be obtained from examination by ^{13}C-NMR of the benzoate end-groups in appropriate polymers prepared using peroxide enriched with carbon-13, as has been done in the case of STY (9). Very significant results about the orientation of attack by benzoyloxy radicals on olefins have also been obtained by the use of radical traps (10). It will be interesting to have results for substances such as benzalacetone in respect of the relative yields of Ph.CO.O.CH(CO.Me).$\dot{\mathrm{C}}$HPh and Ph.CO.O.CHPh.$\dot{\mathrm{C}}$H.CO.Me. If the addition of the radical is subject to thermodynamic control, then the former product can be expected to be favoured because of its greater stability with the unpaired electron on a carbon atom with an attached phenyl group. Several authors (11,12,13) have concluded however that steric and polar effects exert more influence than stabilities of products upon the rates and sites of attack in such reactions. It has been concluded (14) that, in reactions of the 4-chlorophenyl radical with α,β-unsaturated carbonyl compounds, steric considerations are dominant in the governing of regioselectivity.

Those unsaturated carbonyl compounds which exhibit moderate or high reactivities towards the benzoyloxy radical also retard the polymerization of MMA; the magnitude of the effect increases with increasing reactivity of the additive towards the radical. The retardation can be explained by supposing that radicals formed by addition of an initiating or a propagating radical to the additive are comparatively unreactive. Some of the adduct radicals may react with monomer so that polymerization continues but others may undergo termination processes with consequent reduction in the overall rate of polymerization.

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