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Reactivities towards the benzoyloxy radical of monomers with beta-methyl groups

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SUMMARY

Polymers of methyl methacrylate have been prepared at 60°C with benzoyl peroxide as initiator in the presence of methyl tiglate (MT), methyl crotonate (MC) or crotononitrile (CNL); they have been examined for end-groups derived from the initiator. The introduction of beta-methyl groups into methyl methacrylate, methyl acrylate and acrylonitrile (to give MT, MC and CNL respectively) increases reactivity towards the benzoyloxy radical. The effects can be explained in terms of the electron-repelling methyl groups activating the double bonds for reaction with the electrophilic benzoyloxy radical.

INTRODUCTION

At 60°C β-methylstyrene (BMST) is about twice as effective as styrene (STY) in capturing the benzoyloxy radical but, when it is used as a comonomer with methyl methacrylate (MMA), very little is incorporated in the polymer even when [BMST]/[MMA] in the feed is as high as 0.41 (1). Study of the effects of introducing β-methyl groups upon the reactivities of monomers has been extended to methyl tiglate (MT), methyl crotonate (MC) and crotononitrile (CNL), to be regarded as related to MMA, methyl acrylate (MA) and acrylonitrile (AN) respectively.

As previously (1), two procedures are applied, both involving the use of benzoyl peroxide (BPO) to initiate polymerizations of MMA containing MT, MC or CNL and examination of end-groups in the resulting polymers. When the initiator is labelled with carbon-14 in the carbonyl groups and with tritium in the rings, it is possible to determine the ratio of benzoate to phenyl end-groups. The use of BPO enriched with carbon-13 in its carbonyl groups allows direct comparison of the numbers of benzoate groups attached to units derived from the two monomers in a copolymerization. In the first method of

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working, the rate constants for additions of the benzoyloxy radical to the various monomers are compared using the rate constant for the decarboxylation of the radical for reference. In the other method, the rate constants for the additions are compared directly.

EXPERIMENTAL

The experimental procedures were those used in the work involving BMST (1) and in previous studies of the reactivities of unsaturated substances towards the benzoyloxy radical. Commercial samples of MT, MC and CNL were purified by distillation.

RESULTS

The rate of polymerization of MMA, initiated by BPO or azobisisobutyronitrile (AIBN), was hardly affected by the presence of MT at concentrations approximately equal to that of MMA. Under similar conditions, MC caused slight retardation. The presence of CNL considerably reduced the rate of polymerization of MMA but the effect was less than that produced by BMST. Retardation in some of these systems can be explained in terms of degradative transfer, abstraction of hydrogen from the β-methyl group leading to an allylic radical which re-initiates inefficiently.

Polymers of MMA were prepared at 60°C using monomer and $^{14}C,^{3}H$-BPO at concentrations of 3.10 and close to 0.67×10^{-2} mol dm^{-3} respectively, with MT, MC or CNL as a comonomer at a concentration comparable with that of MMA. For each polymer, (^{3}H-activity)/(^{14}C-activity) was measured. The results were used to calculate a fraction $\underline{x}$ given by

$$\frac{\text{no. of benzoate end-groups}}{\text{sum of nos. of benzoate and phenyl end-groups}} =$$

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

where activities are quoted in Bq g^{-1}. Use was then made of the relationship

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

where k_1 is the rate constant for the decarboxylation of the benzoyloxy radical and k_2 and k_2' are the rate constants for addition of the radical to MMA and the comonomer respectively. Results are given in Table 1; the extreme values of k_2'/k_1 correspond to uncertainties of ±5% in the values of $\underline{x}$.

Table 1. Polymerizations initiated by ^{14}C, ^{3}H-Benzoyl peroxide

comonomer	[comonomer]/ [MMA]	(^{3}H-activity)/ ^{14}C-activity for polymer	fraction $\underline{x}$	k_2'/k_1 (mol^{-1}dm^{3})	extreme values of k_2'/k_1 (mol^{-1}dm^{3})
MT	0.71	1.91	0.70	0.58	0.45, 0.75
MC	1.50	2.28	0.57	0.08	0.05, 0.11
MC	1.00	2.46	0.54	0.07	0.02, 0.11
CNL	0.79	2.40	0.55	0.11	0.06, 0.16
CNL	0.56	2.40	0.55	0.15	0.08, 0.23

(^{3}H-activity)/(^{14}C-activity) for peroxide = 1.33

Since k_2/k_1 is 0.31 mol^{-1} dm^{3}, the values of k_2'/k_2 for MT, MC and CNL can be taken as being within the ranges 1.45-2.42, 0.16-0.35 and 0.26-0.52 respectively. In much of the subsequent discussion, rate constants for reactions of unsaturated substances with the benzoyloxy radical are expressed relative to that for the reaction of the radical with STY; it is known that at 60°C the rate constant for the reaction with STY is eight times that for the reaction with MMA.

MMA/MT and MMA/CNL mixtures were polymerized using ^{13}C-BPO and the resulting polymers were examined by 100 MHz ^{13}C-NMR. Figure 1 shows part of the spectrum for the polymer derived from a system in which [MT]/[MMA] was 0.62; it includes the signals arising from the enriched sites in the benzoate end-groups. The benzoate groups attached to units derived from MMA give signals at ca 166.0 and 165.8 ppm; the other peaks at ca 165.6 and

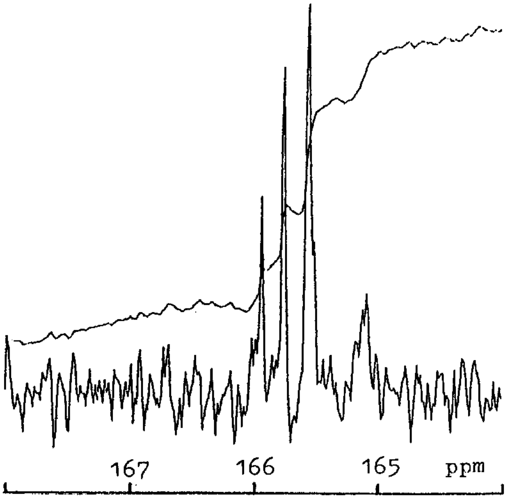

Figure 1. Part of the 100 MHz ^{13}C-NMR spectrum of poly (methyl methacrylate) prepared using ^{13}C-benzoyl peroxide in the presence of methyl tiglate.

165.1 ppm must be associated with benzoate groups adjacent to units derived from MT and they cover an area 1.5 times that for the signals corresponding to the end-groups Ph.CO.O.MMA-. The relationship

$$\frac{\text{area covered by signals due to Ph.CO.O.MT-}}{\text{area covered by signals due to Ph.CO.O.MMA-}} = \frac{k_2'[\text{MT}]}{k_2[\text{MMA}]}$$

leads to k_2'/k_2 as 2.4 with an uncertainty of ±10%, the value of k_2'/k_2 lies within the range for the appropriate polymer referred to in Table 1.

The polymer from a system in which [CNL]/[MMA] was 0.79 gave rise to the signals corresponding to the end-groups Ph.CO.O.MMA-; signals around 165.4 ppm could be assigned to Ph.CO.O.CNL- but they were very small and the spectral noise was such that reliable comparison of areas was not possible.

A polymer recovered from a system in which [MT]/[MMA] was 0.71 and ^{13}C-AIBN was used as initiator was examined by ^{13}C-NMR. The presence of end-groups $Me_2C(CN)$.MMA- was revealed but there was no evidence for the attachment of 1-cyano-1-methylethyl groups to units derived from MT. Evidently MT is much less reactive than MMA towards the $Me_2\dot{C}(CN)$ radical.

DISCUSSION

The relative values of the rate constants for the reactions at 60°C of STY, MMA, MA and AN with the benzoyloxy radical are 1, 0.12, 0.05 and <0.05 respectively, according to procedures involving analyses for end-groups in polymers (2). The corresponding quantities, found by a method depending upon the use of a nitroxide as a radical scavenger (3), are 1, 0.11, 0.02 and 0.02; only in the case of MA is there a significant difference between the results from the two approaches. On the same scale, i.e. using the reaction with STY as the standard, the relative rate constants for the reactions of the benzoyloxy radical with BMST, MT, MC and CNL are 2, 0.23, 0.03 and 0.05. If the lower value is selected for the rate constant in the case of MA, the present results show that, for the four monomers, introduction of a β-methyl group approximately doubles the reactivity of a monomer towards the benzoyloxy radical. If the effects are attributed entirely to change in activation energy, the β-methyl group causes reductions in that quantity of about 2 kJ mol^{-1}.

Tedder and Walton (4), Giese (5) and Fischer (6) have comprehensively reviewed the factors influencing the rates and orientations of the additions of radicals to alkenes. They have concluded that the effects of substituents in the alkenes are not primarily connected with stabilization of the product radicals and that polar and steric effects are of particular importance. For reactions of radicals with unsaturated substances, polar effects are exerted by groups attached to the carbon atom which is not attacked but steric effects are small although of course they may be very important in the subsequent reactions of the adduct radical. Both steric and polar effects can arise from groups attached to the carbon atom with which the attacking radical forms a permanent bond.

In the cases now being considered, there can be little or no difference between the stabilizing effects of the substituents X and Y for the pairs of adduct radicals $R.CH_2.\dot{C}HX/R.CH(CH_3).\dot{C}HX$ and $R.CH_2.\dot{C}XY/R.CH(CH_3).\dot{C}XY$ formed from monomers and their β-methyl counterparts. The introduction of a β-methyl group into a monomer can only increase any steric hindrance to the reaction with a radical. It must be concluded therefore that, for the β-methyl monomers, the electron-repelling methyl group strongly encourages reaction with the electrophilic benzoyloxy radical.

The comparison of the reactivities of unsaturated substances towards the benzoyloxy radical by using $^{14}C,^{3}H$-BPO in polymerizing systems depends upon the assumption that the rate constant for decarboxylation of the radical is unaffected by the nature of the medium; clearly, it cannot be fully justified but there seems to be only one system in which serious error is caused viz. that involving cinnamic acid (7). The method suffers from another limitation in that, by itself, it gives no information on the mode of attachment of the radical to the monomer. The study of benzoate end-groups by NMR spectroscopy requires no assumption about the decarboxylation of the benzoyloxy radical and it can, in principle, distinguish between the products of head- and tail-addition of the radical to the monomer. In the case of STY, the presence in the polymer of a few end-groups $Ph.CO.O.CHPh.CH_2$- was demonstrated (8) and later confirmed (9) but no evidence was found for head-addition of the benzoyloxy radical to MMA (9). The use of radical scavengers (3) has indicated that, for the benzoyloxy radical at 60°C, the ratios of head-addition to tail-addition to STY, MMA, MA and AN are 0.08, 0.07, 0.2 and < 0.03 respectively. There is no reason to suppose that, for the monomers having β-methyl groups, production of $R.CHX.\dot{C}H.CH_3$ or $R.CXY.\dot{C}H.CH_3$ would be favoured.

Giese (5) quoted results showing that, for reaction with the nucleophilic cyclohexyl radical at 20°C, the rate constant for $CHX{:}CH.CO.O.CH_3$ is always considerably less than that for CH_2:CX.CO.O.CH_3, e.g. the rate constant for MMA exceeds that for MC by a factor of about 64. A difference in the same sense, but much smaller at about four, is found for the reactions of the same monomers with the electrophilic benzoyloxy radical. There is an opposite effect for methyl derivatives of STY in their reactions with the benzoyloxy radical, BMST being about twice as reactive as α-methylstyrene (10). The rate constant for the reaction of methacrylonitrile with the benzoyloxy radical is 0.06 (11) relative to that for STY and it is not significantly different from the corresponding quantity now reported for CNL.

Steric hindrance to reactions of a radical with unsaturated substances depends also upon the structure of the radical. In this connection, Fischer (6) has referred to the .$CH(CN)_2$ radical and Giese (5) to the impeding effect of an α-chlorine substituent in the cyclohexyl radical in its reaction with MA. The absence of a detectable reaction between the 1-cyano-1-methylethyl radical and MT can be attributed to the bulky nature of the groups attached to the carbon atom carrying the unpaired electron. The benzoyloxy and other aroyloxy radicals show rather exceptional behaviour not only because of their strongly electrophilic character but also because the unpaired electron on an oxygen atom is not sterically shielded.

Although BMST, MT, MC and CNL are more reactive towards the benzoyloxy radical than the corresponding monomers without β-methyl groups, their reactivities towards the radical are very much less than those of stilbene and related compounds (9) and 1,4-diphenylbuta-1,3-diene (12).

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