Effects of some unsaturated nitrogen-heterocycles on the polymerization of methyl methacrylate initiated by benzoyl peroxide

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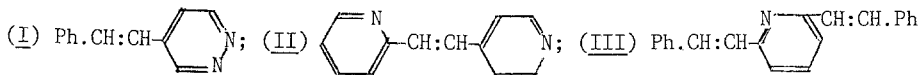[2]School of Physics and Materials, University, Lancaster LA1 4YA, UK

Summary
      The rate of polymerization at 60°C of methyl methacrylate initiated by benzoyl peroxide is almost unaffected by the presence of a small amount of 4-styrylpyridazine, 1-(2-pyridyl)-2-(4-pyridyl)ethylene or 2,6-distyrylpyridine. Examination of polymers made using peroxide suitably labeled with carbon-14 and tritium shows that these additives increase the ratio of benzoate to phenyl end-groups derived from the initiator. This effect arises because the additives are effective in capturing the benzoyloxy radical; in this respect, they are however considerably less reactive than the corresponding compounds containing groups derived from benzene in place of the nitrogen heterocycles.

Introduction
      Stilbene, its derivatives and its hydrocarbon analogues are very effective in capturing the benzoyloxy radical but ordinarily they are quite unreactive as comonomers in radical polymerizations because they show low reactivity towards carbon-centred radicals.(1) As a consequence, when a monomer such as methyl methacrylate (MMA) is polymerized with benzoyl peroxide (BPO) in the presence of a stilbene-like substance at quite low concentration, the resulting polymer contains benzoate end-groups attached to units derived from the additive although the total incorporation of that substance is small. Similar considerations apply when isomers of distyrylbenzene are used as minor constituents in polymerizing systems.(2)
      Introduction of a thienyl group in place of one of the phenyl groups in stilbene, to give 2-styrylthiophene, leads to enhancement of the reactivity towards the benzoyloxy radical by a factor of about 7·5;(3) 4-styrylpyridine is however less reactive than stilbene by a factor of about five.(4) We now report the reactivities of other substances in which nitrogen-containing rings replace phenyl groups in stilbene or distyrylbenzene; the substances considered are 4-styrylpyridazine ($\underline{I}$), 1-(2-pyridyl)-2-(4-pyridyl)ethylene ($\underline{II}$) and 2,6-distyrylpyridine ($\underline{III}$).

($\underline{I}$) Ph.CH:CH—⟨ring⟩N; ($\underline{II}$) ⟨ring⟩—CH:CH—⟨ring⟩N; ($\underline{III}$) Ph.CH:CH—⟨ring⟩CH:CH.Ph

      It has been shown already, by a method involving examination by ^{13}C-NMR of polymers made using ^{13}C-enriched BPO, that ($\underline{III}$) is reactive towards the benzoyloxy radical;(4) for that particular additive, however, it was not possible to make quantitative measurements. In the present work, the reactivities of ($\underline{I}$) – ($\underline{III}$) towards the benzoyloxy radical were assessed by the method depending upon the use of BPO labeled with tritiated phenyl rings and with carbon-14 at the carbonyl sites. The use of this type of BPO, referred

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to as *BPO, makes it possible to compare the numbers of benzoate and phenyl end-groups in a polymer.

Experimental

Standard procedures were used for the purification of monomeric MMA and the preparation of *BPO. The E-isomers of 4-styrylpyridazine (Lancaster Synthesis) and 1-(2-pyridyl)-2-(4-pyridyl)ethylene (Aldrich) were used as received; the E,E-isomer of 2,6-distyrylpyridine (donated by Synthetic Chemicals Ltd.) was recrystallized from benzene/methanol. Polymerizations were performed at 60°C under air-free conditions with toluene as diluent; rates were monitored dilatometrically and conversions were limited to 8%. Each polymer was recovered and purified by three precipitations in methanol. The assays for carbon-14 and tritium were made by scintillation counting of solutions.

Results

The nitrogen-containing additives considered here had very little influence on the rate of polymerization of MMA, at least at concentrations up to those shown in Table 1 which refers to polymerizations initiated by *BPO and to the recovered polymers.

Table 1. Polymerizations of MMA initiated by *BPO in the presence nitrogen-containing additives

Expt. no.	[MMA] mol dm^{-3}	10^2[BPO] mol dm^{-3}	10^2[additive] mol dm^{-3}	specific activities of polymer in Bq g^{-1}	
				carbon-14	tritium
1	2·95	0·53	2·11 (I)	85·2	585
2	3·15	0·54	4·13 (I)	115·5	721
3	3·05	0·52	6·12 (II)	95·3	627
4	3·05	0·53	3·60 (III)	88·2	537
5	3·05	0·52	–	71·5	502

specific activities of *BPO :– 2·87 x 10^5 and 9·78 x 10^5 Bq g^{-1} for carbon-14 and tritium respectively
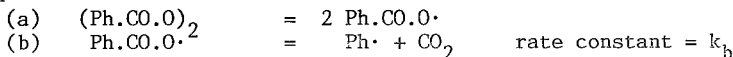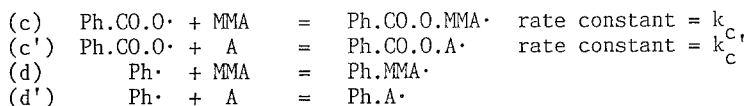
Discussion

When *BPO is used as initiator, both the benzoate and phenyl end-groups in the resulting polymer are labelled with tritium but only the benzoate end-groups contain carbon-14. A fraction x for a polymer is defined as (no. of benzoate end-groups)/(sum of nos. of benzoate and phenyl end-groups) so that $x/(1-x)$ is equal to (no. of benzoate end-groups)/(no. of phenyl end-groups). For a polymer prepared using *BPO, x can be calculated by means of the expression

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

From the data in Table 1, it is found that the values of x for polymers (1)–(5) are 0·504, 0·546, 0·518, 0·560 and 0·486 respectively. It is plain that each of the three additives, when present in the polymerizing system, causes an appreciable increase in the ratio of benzoate to phenyl end-groups in the resulting polymer.

Reactions (a)-(d') must be considered in connection with the initiation of the polymerization of MMA by BPO in the presence of an unsaturated additive A

(a) $(Ph.CO.O)_2$ $=$ 2 Ph.CO.O·

(b) Ph.CO.O· $=$ Ph· + CO$_2$ rate constant $= k_b$

(c) Ph.CO.O· + MMA = Ph.CO.O.MMA· rate constant = k_c

(c') Ph.CO.O· + A = Ph.CO.O.A· rate constant = k_c'

(d) Ph· + MMA = Ph.MMA·

(d') Ph· + A = Ph.A·

Analysis of the competition between reactions (b), (c) and (c') leads to the equation $x/(1-x) = k_c[MMA]/k_b + k_c'[A]/k_b$ where, for the systems under consideration, A represents (I), (II) or (III). Previous work has shown that k_c/k_b can be taken as $0 \cdot 31$ mol^{-1} dm^3 and the same value is obtained from the results for expt.(5). Use of the values of x for polymers (1)-(4) and of [MMA] and [A] for the systems and application of the equation shown above makes it possible to evaluate k_c'/k_b for each of the additives; then their reactivities towards the benzoyloxy radical can be compared with that of MMA by means of the quantities k_c'/k_c.

Table 2 shows the values of k_c'/k_c for the E-isomer of stilbene, for various isomers of distyrylbenzene and for 4-styrylpyridine as previously found (4) and also the results now obtained for the E-isomers of unsaturated substances containing groups derived from nitrogen-heterocycles.

Table 2. Reactivities towards the benzoyloxy radical

compound	k_c'/k_c	compound	k_c'/k_c
(i) stilbene	40	(vi) 4-styrylpyridine	8
(ii) E,E-1,4-distyrylbenzene	450	(vii) 4-styrylpyridazine	11, 17
(iii) E,Z-1,4-distyrylbenzene	170	(viii) 1-(2-pyridyl)-2-(4-	
(iv) Z,Z-1,4-distyrylbenzene	105	pyridyl)ethylene	7
(v) E,E-1,3-distyrylbenzene	84	(ix) 2,6-distyrylpyridine	29

There is quite a large difference between the two values of k_c'/k_c for (vii) but, as explained previously, the determinations are susceptible to considerable uncertainty when dealing with additives of comparatively low reactivity; the differences between the results for (vi), (vii) and (viii) may therefore not be significant. Comparison of the value for (i) with those for (vi), (vii) and (viii) shows clearly however that marked reduction in reactivity towards the benzoyloxy radical is caused by replacement of phenyl groups in stilbene by groups derived from nitrogen-heterocycles. For consideration of the reactivity of (ix), it is necessary to note the great differences between the reactivities of isomers of distyrylbenzene. It seems to be reasonable to compare (ix) with (v), the least reactive of those isomers of distyrylbenzene which have been examined; on that basis, it is found again that replacement of a benzene residue by a pyridine residue is accompanied by an appreciable reduction in reactivity towards the benzoyloxy radical.

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