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THE REACTIVITY OF α -METHOXYSTYRENE TOWARD THE BENZOYLOXY RADICAL: END GROUPS OF COPOLYMERS OF α -METHOXYSTYRENE WITH METHYL METHACRYLATE

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ABSTRACT

Use has been made of procedures involving ^{13}C -enriched benzoyl peroxide or alternatively peroxide labeled with carbon-14 and tritium for study of end groups in copolymers of α -methoxystyrene with methyl methacrylate. It has been shown that α -methoxystyrene is very reactive toward the benzyloxy radical. Induced decomposition of benzoyl peroxide is significant in systems containing α -methoxystyrene.

INTRODUCTION

The ceiling temperature for the polymerization of α -methoxystyrene (MOS) is very low [1], but the monomer engages in radical copolymerization with

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styrene (STY), acrylonitrile, methyl acrylate, and methyl methacrylate (MMA), and its reactivity toward the 1-cyano-1-methylethyl (or 2-cyano-2-propyl) radical at 60 and 100°C is comparable with that of MMA [2]. The values of Q and e for MOS have been given [1] as 0.65 and -1.20, respectively. The comparatively large and negative value of e suggests that the monomer should be rather reactive toward the benzoyloxy radical [3]. To test this prediction, studies of the end groups for copolymers of MOS with MMA have been made at 60°C with benzoyl peroxide (BPO) as initiator.

In the first procedure, [^{13}C -carbonyl] benzoyl peroxide (^{13}C -BPO) was used with the intention of comparing the numbers of $\text{C}_6\text{H}_5\text{COO-MOS-}$ and $\text{C}_6\text{H}_5\text{COO-MMA-}$ end groups by examination of the ^{13}C -NMR spectra of the copolymers. In the second method of working, use was made of BPO labeled at the carbonyl sites with carbon-14 and in the rings with tritium (^{14}C , ^3H -BPO); assays of the peroxide and the copolymers then allowed comparisons of the numbers of benzoate and phenyl end-groups to be made. The first procedure involved study of the competition between the two monomers for capture of benzoyloxy radicals; the second depended upon the competition between those reactions and the decarboxylation of the benzoyloxy radical.

EXPERIMENTAL

Preparations of materials and most of the experimental procedures were described previously [2, 4]. Polymerizations were performed at 60°C with toluene as diluent and were monitored dilatometrically; conversions did not exceed 8%. Polymers were recovered by precipitation in methanol and purified by reprecipitation (twice when ^{14}C , ^{13}H -BPO had been used). The specific activities with respect to carbon-14 and tritium were determined with an LKB-Wallac "Spectral" 1219 liquid-scintillation counter. Weighed samples were dissolved in a toluene-butylPBD scintillator mixture. Corrections for quenching were made by the spectral quench parameter method with an external standard. This method uses the calibrated shift of the external standard spectrum for each sample as a means of determining the efficiency of counting of each radionuclide in its respective counting channel.

RESULTS

The copolymerizations of MOS with MMA initiated by BPO were slow, and the required conversions were reached only after long periods at 60°C. The rates fell off quite noticeably with time (see Fig. 1); a similar effect was

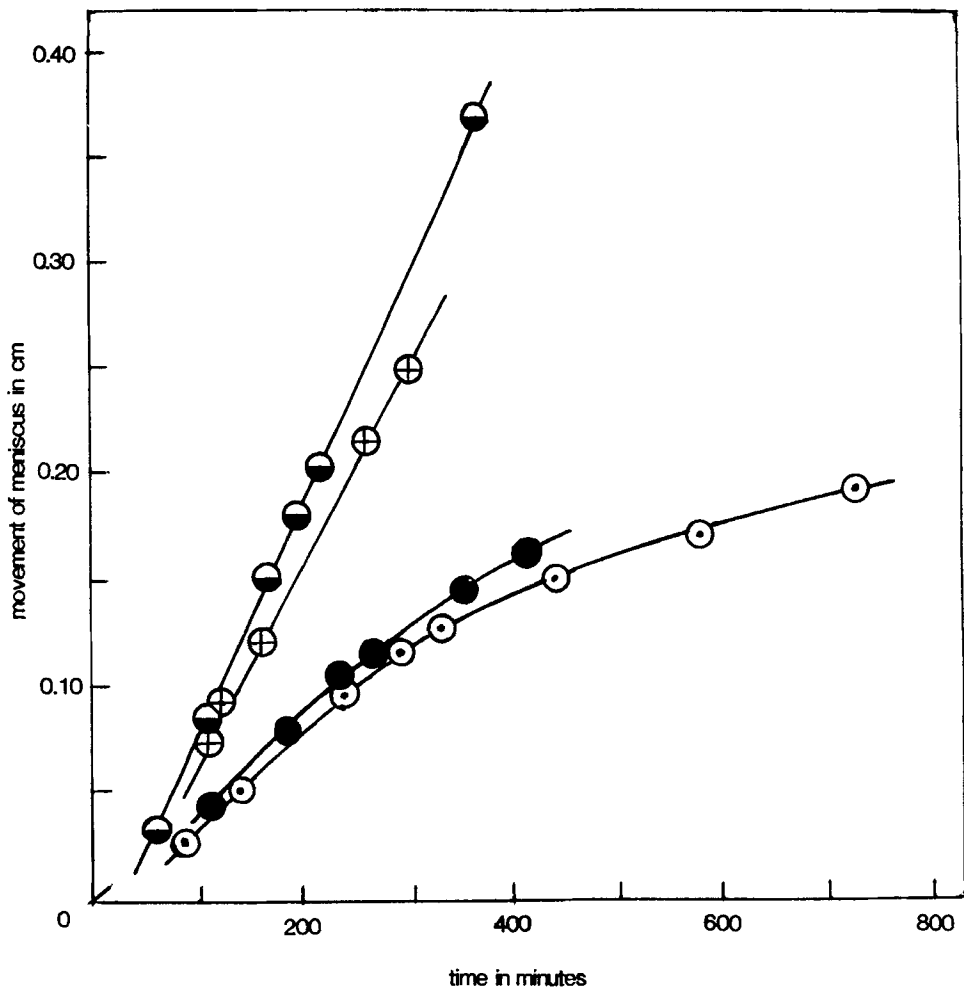


FIG. 1. Contraction vs time plots for a set of polymerizations in a particular dilatometer; concentrations shown in mol/L. ○: [BPO] = 0.0063; [MOS] = 0.61; [MMA] = 3.10. ●: [BPO] = 0.0095; [MOS] = 0.48; [STY] = 3.33. ⊕: [BPO] = 0.0108; [STY] = 3.33. ◐: [AIBN] = 0.0114; [MOS] = 0.48; [STY] = 3.33.

found when STY replaced MMA but not when azobis(isobutyronitrile) (AIBN) was used instead of the peroxide, even though normally the rate of decomposition of AIBN at 60°C is greater than that of BPO at that temperature. The

TABLE 1. Polymerizations Initiated by Benzoyl Peroxide

Polymer no.	Concentrations, mol/L			$10^{-3} \times$ specific activity of polymer, Bq/g	
	BPO	MOS	MMA	Carbon-14	Tritium
1 ^a	0.0134	1.70	2.34	—	—
2 ^a	0.0173	0.85	4.21	—	—
3 ^b	0.0052	0.83	4.20	1.08	1.58
4 ^b	0.0069	0.32	5.65	2.18	3.36
5 ^b	0.0042	0	2.42	0.22	0.68

^aBPO enriched with carbon-13.

^bBPO labeled with carbon-14 and tritium; $10^{-6} \times$ specific activity in Bq/g: carbon-14, 0.83; tritium, 1.10.

initial rate of polymerization decreased as $[MOS]/[MMA]$ in the feed was increased.

Copolymerizations of MOS with MMA, using ^{13}C -BPO or ^{14}C , 3H -BPO, are referred to in Table 1. Parts of the 25 MHz ^{13}C -NMR spectra of Polymers 1 and 2 are shown in Fig. 2; the signals arise from the enriched carbonyl sites in benzoate end-groups. There are no clear indications that the spectra of these copolymers contain signals which could be attributed to C_6H_5COO -MMA-groups; such signals are found at δ 165.8 and 165.5 [4] and to some extent would be overlaid by the main component.

The specific activities of Polymers 3, 4, and 5 of the peroxide can be used to calculate the ratio (No. of benzoate end-groups)/(No. of phenyl end-groups) by using the relationship [5]

$$\frac{\text{no. of benzoate end-groups}}{\text{no. of benzoate + phenyl end-groups}} = x$$

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

The values of x for Polymers 3, 4, and 5 are 0.91, 0.86, and 0.43, respectively. Use is then made of the relationship [6]

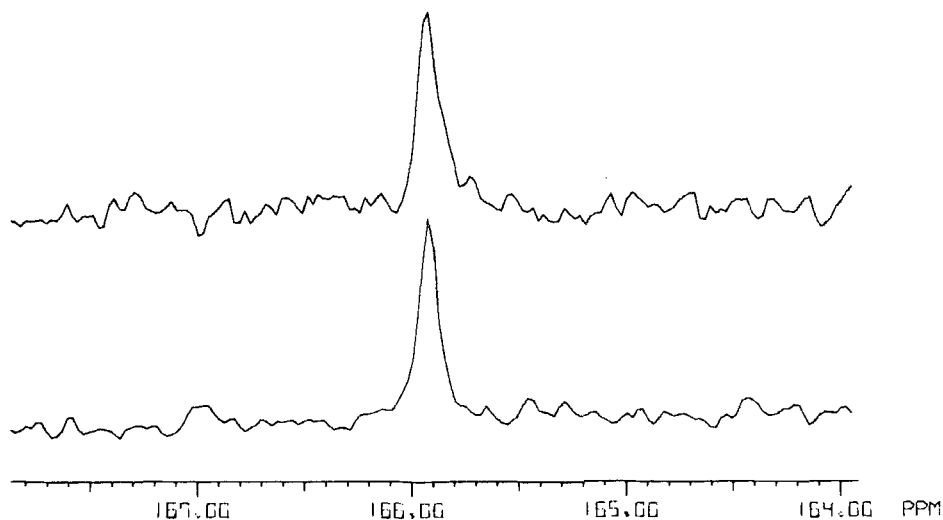


FIG. 2. 25 MHz ^{13}C -NMR spectra for copolymers of MOS with MMA prepared by using ^{13}C -BPO. Upper spectrum, Polymer 1; lower spectrum, Polymer 2 (see Table 1).

$$\frac{x}{1-x} = \frac{\text{no. of benzoate end-groups}}{\text{no. of phenyl end-groups}} = \frac{k_2' [\text{MMA}]}{k_1} + \frac{k_2 [\text{MOS}]}{k_1},$$

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 MOS and MMA, respectively. The results for Polymer 5, a homopolymer of MMA, give k_2'/k_1 as $0.31 \text{ mol}^{-1} \cdot \text{dm}^3$, in good agreement with a much older value [7]. Values of k_2/k_1 of 10.6 and $13.7 \text{ mol}^{-1} \cdot \text{dm}^3$ are found for Polymers 3 and 4, respectively.

The tritium activity of a polymer prepared from $^{14}\text{C}, ^3\text{H}$ -BPO can be used to calculate the number of monomeric units accompanying each initiator fragment incorporated in the polymer. The composition of a copolymer of MOS with MMA, prepared with BPO as initiator, can be represented thus:



where f is unity for Polymer 5 since it is a homopolymer of MMA. Monomer reactivity ratios for the copolymerization of MMA (Monomer 1) with MOS

have been given [1] as $r_1 = 2.5$ and $r_2 = 0$, so that the calculated values of f for Polymers 3 and 4 are 0.93 and 0.98, respectively, and the average monomeric units can be represented as $C_{5.28}H_{8.14}O_{1.93}$ and $C_{5.08}H_{8.04}O_{1.98}$, with formula weights of 102 and 101, respectively. The tritium content of a phenyl end-group is the same as that of a benzoate end-group, and the difference in mass is negligible compared with that of the polymer chain; each polymer can therefore be represented as $(C_6H_5COO)_1$ (average monomeric unit) $_n$, so that

$$\frac{{}^3\text{H-specific activity of polymer}}{{}^3\text{H-specific activity of peroxide}} = \frac{121}{121 + wn},$$

where w is the formula weight of the average monomeric unit. Using the specific activities given in Table 1, the calculated values of n for Polymers 3, 4, and 5 are 829, 394, and 1964, respectively. These results are little affected by the precise values selected for the monomer reactivity ratios required to calculate the compositions of copolymers; if Polymers 3 and 4 are treated as pure polyMMA, the derived values of n are 845 and 398.

It is necessary to consider possible effects of loss of material of comparatively low molecular weight during recovery and purification of a polymer; such material would be expected to be rich in end groups so that the ${}^3\text{H}$ - and ${}^{14}\text{C}$ -activities of the recovered polymer would be lower than those of the whole polymer, and therefore the value of n based on the ${}^3\text{H}$ -activity would be higher than the true value. On the other hand, calculations based on the ratio of the ${}^3\text{H}$ - and ${}^{14}\text{C}$ -activities are most probably unaffected by any loss of polymer since the ratio of benzoate to phenyl end-groups is expected to be the same in all fractions of the polymer.

DISCUSSION

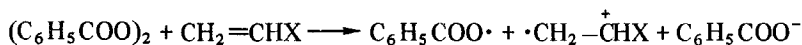
The two values of k_2/k_1 for MOS are not in as good agreement as would be expected, but values around $12 \text{ mol}^{-1} \cdot \text{dm}^3$ are considerably greater than those for STY ($2.50 \text{ mol}^{-1} \cdot \text{dm}^3$) and MMA ($0.31 \text{ mol}^{-1} \cdot \text{dm}^3$) and are in the region reasonable for a monomer having a value of e of -1.2 [3]. It is possible, from values of k_2/k_1 and k_2'/k_1 , to predict the relative areas under the peaks in the ${}^{13}\text{C}$ -NMR spectra corresponding to the enriched end groups $C_6H_5COO\text{--}MOS\text{--}$ and $C_6H_5COO\text{--}MMA\text{--}$ in copolymers of MOS with MMA. The required relationship is

$$\frac{\text{area for } C_6H_5COO-MOS-}{\text{area for } C_6H_5COO-MMA-} = \frac{12[MOS]}{0.31[MMA]},$$

where [MOS] and [MMA] are the concentrations in the copolymerizing system. The predicted ratios of areas for Polymers 1 and 2 are 30:1 and 8:1, respectively. The enriched carbonyl atom in $C_6H_5COO-MMA-$ gives peaks of comparable heights at δ 165.8 and 165.5, and there is no direct evidence for their presence even for Polymer 2, which was prepared from a system in which [MOS]/[MMA] was considerably less than that which led to Polymer 1. The present NMR study of benzoate end-groups is inconclusive, but it suggests that MOS is much more reactive than MMA toward the benzoyloxy radical.

It is significant that rates of polymerizations involving MOS decreased markedly with conversion when BPO was the initiator. The monomer reactivity ratios for MMA with MOS have been quoted already; very similar values have been given [1] for STY (Monomer 1) with MOS, viz., $r_1 = 2.7$ and $r_2 = 0$. In copolymerizations of MOS with MMA or STY, the nonethereal monomer is consumed preferentially, so that the relative concentration of MOS gradually increases. This effect by itself might cause the change in the rate of polymerization. This explanation must be rejected because the decrease in rate was not observed for systems in which AIBN was the initiator. Evidently the conversions were insufficient for any effect due to drift in the composition of the feed to become apparent. It is considered that the decrease in rate was caused by depletion in BPO resulting from enhancement in the rate of consumption of the peroxide, brought about by the presence of MOS. Induced decompositions of BPO occur in ethereal solvents [8] and in inert solvents also containing poly-(*p*-methoxystyrene) or *p*-ethylanisole [9], but induced decompositions of AIBN have not been reported.

Anomalies also arise in the polymerization of *N*-vinylcarbazole initiated by BPO, but not when AIBN is used. The polymer formed in the presence of BPO appears to contain only a small amount made by a radical process [10]. It is believed that there is an interaction of the monomer and the peroxide [11] according to the scheme



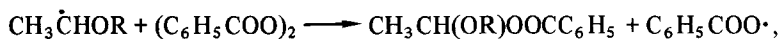
and that most of the polymer is formed by a cationic process. There is no evidence for an effect of this type for *p*-methoxystyrene or MOS, and indeed, a cationic copolymerization could not occur for MMA with MOS as comonomer.

There are some puzzling aspects of the present results on the number (n) of monomeric units for each incorporated fragment derived from BPO. It is anomalous that n for Polymer 3 should be so much greater than for Polymer 4. The difference between the concentrations of BPO used for the two copolymerizations is quite insufficient to account for the discrepancy. As explained already, loss of small polymer molecules during recovery and purification would have an effect, but it is most unlikely that it could be responsible for the large difference between the values of n for Polymers 3 and 4.

It must be recognized that the polymers listed in Table 1 are likely to contain end groups of various types in addition to those derived from BPO. The reaction leading to Polymer 5, a homopolymer of MMA, most probably involved disproportionation as the dominant mode of termination, giving rise to end groups $-\text{CH}_2\text{CH}(\text{COOCH}_3)\text{CH}_3$, $-\text{CH}=\text{C}(\text{COOCH}_3)\text{CH}_3$, and $-\text{CH}_2\text{C}(\text{COOCH}_3)=\text{CH}_2$. The value of n , deduced from analysis for initiator fragments, must therefore be almost doubled to give the average degree of polymerization. It is suggested that Polymers 3 and 4 contain many end groups not derived from BPO and that the proportion for Polymer 3 is higher than for Polymer 4, so leading to the difference between the values of n for the two polymers. The explanation of the anomaly may be connected with the effect of MOS upon the decomposition of BPO. Walling [8] summarized views on the decomposition of BPO promoted by ethers. It is believed [12] that reaction of the benzoyloxy radical with an ether,



is followed by attack of the product radical upon a molecule of BPO,



and that a chain reaction can develop. When a polymerizable monomer is present, the chain may be interrupted. Clearly, however, some induced decomposition occurs in the presence of mixtures of MOS with MMA because the rate of polymerization falls off more quickly than expected. It is now suggested that the benzoyloxy radical can interact quite readily with MOS to give a radical corresponding to $\text{CH}_3\dot{\text{C}}\text{HOR}$, perhaps $\text{CH}_2=\text{C}(\text{C}_6\text{H}_5)\text{OCH}_2\cdot$, and that short decomposition chains may follow. It is further suggested that some of the end groups in the resulting copolymer of MOS with MMA are formed by initiation or termination involving the radical derived from MOS. These ideas are as yet untested but further work is in progress.

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