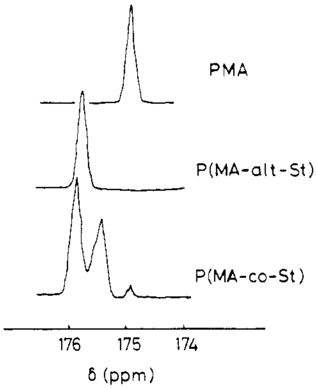

Figure 2. Carbonyl carbon part of ^{13}C NMR spectra of PMA, P(MA-*alt*-St), and a random copolymer (f_M = 47.2 mol %).

from lower magnetic field, where M and S denote, respectively, MA and St units. Inversion–recovery measurements revealed that the ^{13}C species corresponding to these three carbonyl peaks had the same spin–lattice relaxation time, 2.4 s, when measured in 10 w/v % $CDCl_3$ solution at 33 °C. Further, the relative intensities of these triplet peaks were confirmed to be in good agreement with the contents of the above triad sequences calculated on the conventional radical copolymerization mechanism. This direct correlation between the relative intensities of triplet carbonyl carbon resonance and the sequential triad contents calculated hold generally for random MA–St copolymers with various compositions. Representative data are given in Table II. Thus, the distribution of triad monomer sequences in MA–St copolymers can be quantitatively and easily determined from the split peaks of the carbonyl carbon resonance.

The NMR signals of the other carbons in the copolymer provide little information about the microstructure. The equimolar copolymer obtained in the presence of metal halides showed a singlet at 39.2 ppm, the chemical shift just in the middle between those for the methylene carbons in PMA (34.9 ppm) and in PSt (43–44 ppm, broad). This equivalence of the two methylene carbons, one originating from MA and the other from a St unit, should also be attributed to the alternating sequence structure. In addition to this singlet, which is assigned to the methylene carbon in the MA–St dyad and which is not affected by cotacticity, two methylene signals of MA–MA and St–St dyads appear in the spectra of random copolymers at the same positions as for the methylenes in PMA and PSt, respectively. However, the partial overlapping of these signals with the signals at 40–42 ppm due to the methine carbons in both monomer units makes it difficult to measure the dyad sequence distribution with adequate reliability.

Acknowledgment. This work was supported by a Grant-in-Aid for the Contribution to Industrial Technology from the Asahi Glass Foundation.

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Products of Oxidation of Styrene

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Received December 29, 1980

This note integrates the results of a paper by Mayo[1] (designated by M, often with section numbers) and one by Cais and Bovey[2] (designated by C&B, often with page numbers) on the products of oxidation of styrene. It shows that most of the differences in the conclusions in the two papers are associated with the different oxygen pressures used and the products taken for study. The C&B work is based on ^{13}C NMR studies of poly(styrene peroxides) made at 15 and 760 torr of oxygen and then precipitated several times from benzene with methanol. Thus the 55% yields of benzaldehyde and styrene oxide that M-4.1 reported at 15 torr and the methanol-soluble polymer were neglected. M-2.2 analyzed the whole polymers, mostly by C and H with O by difference but sometimes also by peroxide determinations (M-2.7), although both methods have limitations. Benzaldehyde and styrene oxide were determined separately. M carried out oxidations at 50 °C and oxygen pressures from 0.19 to 3200 torr. C&B determined the structures of their two copolymers by ^{13}C NMR.

Excess Methylene Groups

From several lines of evidence, M-2.7 and -4.5 concluded that copolymers made at the lowest oxygen pressures contained methylene groups left from incomplete decomposition of polyperoxide into benzaldehyde and formaldehyde. The H/C ratio in styrene and its polyperoxide is 1.000; in $C_8H_8 + CH_2$ and its polyperoxides it is 1.111. The best evidence for excess methylene groups in styrene polyperoxide is the H/C ratio of 1.07_9 in M-Table II for the polymer made at 1.1 torr of oxygen. The 1.03_6 ratios in copolymers made at 15 and 740 torr suggest excess methylene groups but this discrepancy is not well beyond experimental error. Further evidence for methylene groups comes from M-4.5 and M-Table II. These show that two copolymers contained peroxide groups that did not give benzaldehyde on pyrolysis. However, the evidence for $-CH_2-O-$ groups in poly(α-methylstyrene peroxide) made at low pressure (M-8.5) is compelling; although polymers made at high and low oxygen pressures have nearly the same C:H:O ratios, the former is a polyperoxide but the latter is not; it apparently contains $-C_9H_{10}-O-$ and $-CH_2-O-$ groups. C&B are confident that $-O-CH_2-O-$ groups were absent in their 15-torr copolymer but are less confident about the absence of $-CH_2-CHPh-CH_2-O_2-$ groups. We conclude that the proportion of excess methylene groups is low and uncertain in the 15-torr polymer but becomes significant at lower pressures.

Further, there is a discrepancy between the M and C&B copolymers made at 15 torr when their compositions are expressed on the same basis. The M copolymer contained 1.18 C_8H_8/O_2 (counting two ether links as one peroxide link) and contained 73.2% C. From the chain composition of the C&B polymer on p 173, the C_8H_8/O_2 ratio is 1.38_3, corresponding to 75.49% C, which is significantly different from the M value. An elemental analysis of the C&B copolymer is desirable to support their conclusions. The difference between the two copolymers may be the result

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Table I
Monomer Reactivity Ratios for Reactions of Styrene Radicals with Different Penultimate Groups with Oxygen

	C&B[2]	M[1]
r for $-S-S\cdot$	5.2×10^{-6}	4.4×10^{-8}
r for $-O_2-S\cdot$	3×10^{-6}	1.8×10^{-6} to 3.3×10^{-7}
r for $-O-S\cdot$	6.4×10^{-6}	8.0×10^{-7} preferred

of rejection of the low molecular weight, higher oxygen copolymers by C&B.

Monomer Reactivity Ratios

The next point for discussion is the values of the monomer reactivity ratios (MRR, r) for radicals ending in a styrene unit, i.e., the ratio of the rate constants for the reaction of this radical with styrene monomer and with oxygen, respectively. M-4.5 shows that this ratio is constant from 760 down to about 15 torr of oxygen but then decreases sharply, possibly becoming nearly constant again below 2 torr. This change in MRR was accounted for (M-4.5) by postulating that it had two values, one for a styrene radical with a penultimate peroxide group (predominating at high oxygen pressures) and one for a styrene with a penultimate styrene unit (predominating at very low oxygen pressures). The MRR's were estimated by three slightly different methods; the results are in Table I. All methods gave the same r_{SS}, but $r_{\mathrm{O_2S}}$ varied considerably. The simplest interpretation of this difference is that the $-MM\cdot$ radical reacts faster than the $-O_2M\cdot$ radical with oxygen, a difference consistent with several other copolymerization and chain transfer reactions (M-4.5). Bamford and Basahel[3] recently reported a similar effect of penultimate methyl acrylate units in chain transfer of styrene with CBr_4. Their paper appears to establish the existence of a penultimate effect without any need for involving complexing.

In determining MRR's, the M treatment includes the benzaldehyde and styrene oxide formed as having been incorporated temporarily in the growing polymer radical. Although some account was taken of the presence of ether and excess methylene groups in the copolymer, the MRR calculations are based mostly on the total oxygen in the copolymer, as if the latter contained only C_8H_8 and O_2 units. The C&B treatment neglects the contributions of all the methanol-soluble materials but calculates MRR's for styrene units with penultimate styrene, $-O_2-$, and $-O-$ units. However, the MRR's based on their copolymer made at 15 torr do not accurately predict the sequence distribution in the copolymer made at 1 atm of oxygen. Table I shows that M's upper limit of r for $-O_2-S\cdot$ approaches that of C&B, but that the values for $r_{\mathrm{SS\cdot}}$ differ by about 100-fold. We conclude that there is probably a substantial penultimate effect as reported by M, but his failure to resolve effects of $-O-S\cdot$ and $-O_2-S\cdot$ radicals render his results quantitatively unsatisfactory. The C&B results are based on reprecipitated polymer and therefore neglect more than half of the styrene that was temporarily incorporated in growing radicals.

End Groups

We agree that most of the polyperoxide molecules formed at 1 atm of oxygen are the result of chain transfer. M-5 indicates that 20–25 molecules of polyperoxide are formed per AIBN decomposed, i.e., 16–21 per initiating radical at 60% efficiency of initiation, in good agreement with the C&B finding of one AIBN fragment per 16 chains. Although C&B have made a new contribution on end groups, their conclusions (p 174) leave unsolved problems. The most serious of these is their finding of about 0.67 benzoyl (Bz) groups per chain, in addition to about 0.33 benzoylperoxy ($BzO_2\cdot$) groups per chain.

We can account for only 0.14 Bz groups per chain to balance the $-CH_2-CHPh-OH$ group formed in the Russell termination mechanism. We agree that benzaldehyde, formed from the polyperoxide radical, accounts for chain transfer after a moderate conversion, but it cannot contribute to chain transfer in the earliest stages of the oxidation. Further, this transfer would produce $BzO_2\cdot$ end groups at the beginning of the next chain. The excess Bz groups might come from decomposition of $-CH_2-CHPh-O_2H$ end groups. An obvious source of these groups is transfer of peroxy radical with benzaldehyde, but then formation of additional BzO_2 groups would be required. We can hardly propose oxidation of $-CH_2-CHPh-OH$ or more benzoyl groups by chain termination; we already have too much termination for the AIBN end fragments found. Additional $HO_2\cdot$ end groups could be formed by reaction 42 in M-5, where a terminal styrene radical, instead of adding oxygen, donates an α-hydrogen atom to the oxygen, leaving a terminal $-CH{=}CHPh$ group (not considered by C&B) and an initiating $HO_2\cdot$ group. However, decomposition of this hydroperoxide group would not give the required Bz group. Probably the end group and chain transfer problems cannot be solved without consideration of all the end groups, most of which may be in the lost low polymer.

Conclusions

This note has reviewed the present status of problems associated with the presence of excess methylene groups, estimation of monomer reactivity ratios, and end groups in the oxidation of styrene to polyperoxide. Needs for further work to resolve these problems are indicated. We add here a new explanation for the formation of benzaldehyde and formaldehyde in the pressure-independent cleavage of polyperoxide at high oxygen pressures. Nonterminating interactions of peroxy radicals have been well established[4,5] since the Mayo papers were written. They now appear to offer the best explanations for the formation of aldehydes from styrene and for acetophenone from α-methylstyrene at high oxygen pressures:

$$2\ -S-O_2-S-O_2\cdot \rightarrow 2\ -S-O_2-S-O\cdot + O_2$$

The resulting alkoxy radicals then decompose at once to the carbonyl compounds.

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Continuous Method To Determine Solubility in Polymer Blends

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Received December 19, 1980

Introduction

Polymer blends have drawn considerable attention in recent years because combining existing polymers may give

0024-9297/81/2214-0886$01.25/0