The Mechanisms of Retardation and Inhibition in Radical Polymerizations. Part II.* The Effects of p-Benzoquinone upon the Sensitized Polymerization of Styrene.

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The effects of *p*-benzoquinone upon the sensitized polymerization of styrene at 60° have been studied in detail by using [¹⁴C]benzoquinone and azo[¹⁴C]*iso*butyronitrile as sensitizer. There is initially a slow polymerization, during which all the *p*-benzoquinone is consumed and polymer of low molecular weight is produced; the slow reaction changes fairly abruptly to a fast reaction which has all the characteristics of the normal polymerization. During the slow reaction most of the quinone becomes incorporated in the polymer although a small amount of it reacts directly with the radicals produced from the sensitizer.

IN this paper a study of the effects of *p*-benzoquinone upon the bulk polymerization of styrene initiated by azo*iso*butyronitrile is reported. The work involved the use of [¹⁴C]*p*-benzoquinone and azo[¹⁴C]*iso*butyronitrile; these substances had already been used in a study of the effect of the quinone upon the polymerization of methyl methacrylate (Bevington, Ghanem, and Melville, *Trans. Faraday Soc.*, 1955, in the press).

The main uses of methods involving labelled reagents in a study of this sort can be summarized as follows : (i) It is possible to see if a particular substance becomes chemically incorporated in polymer; then if the number-average molecular weight of the polymer is known, the exact amount of the substance combined in each polymer molecule can be calculated.

(ii) By means of isotope dilution analysis, it is possible to decide what substances of low molecular weight are formed during the polymerization, and also to determine their exact yields.

(iii) If an abnormality is introduced into the regular structure of a polymer, *e.g.*, if a molecule of *p*-benzoquinone is incorporated in a polystyrene chain, it may be possible to find the way in which it is linked. Suppose that the abnormal unit in the structure is radioactive and that the polymer is then treated with chemical reagents which cleave specific linkages. If a particular reagent causes the activity to be lost from the polymer, it is likely that the abnormality is bound into the polymer by a certain type of chemical linkage.

(iv) The rates of initiation in radical polymerizations can be found by a straightforward method using labelled initiator (Bevington, Bradbury, and Burnett, *J. Polymer Sci.*, 1954, **12**, 469); reaction involving an added substance may be revealed by study of rates of initiation.

Information obtained in these ways can lead to a full understanding of the mechanisms by which additives affect polymerizations. In theory it would be possible to obtain this information by conventional analytical methods, but in practice the small weights of the substances involved and the complexities of the mixtures combine to make isotopic methods essential.

The effects of *p*-benzoquinone upon the sensitized polymerizations of styrene and methyl methacrylate appear to be very different. It is shown in this paper, however, that the differences are not fundamental, and an attempt is made to account for them in terms of the relative reactivities of styrene and methyl methacrylate and of the corresponding radicals.

EXPERIMENTAL

Materials.—Descriptions have been given for the procedures used in the purification of monomer and solvents, and in the preparation of azo[¹⁴C]*iso*butyronitrile, tetramethylsuccinonitrile, and [¹⁴C]*p*-benzoquinone (Bevington, Melville, and Taylor, *J. Polymer Sci.*, 1954, **12**,

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449; Bevington, *J.*, 1954, 3707; Bevington, Ghanem, and Melville, *loc. cit.*). The diether $C_6H_4(O \cdot CMe_2 \cdot CN)_2$ was prepared by the method described by Bickel and Waters (*J.*, 1950, 1764). The diacetate of quinol was prepared from quinol and acetic anhydride and recrystallized from ethanol. Quinol was recrystallized from water.

Methods.—Reaction tubes were charged with initiator, *p*-benzoquinone, and monomer and degassed as described previously. The polymerizations were followed dilatometrically; it was supposed that, at 60°, 17·58% contraction is equivalent to 100% polymerization. Polymers were isolated and reprecipitated as described for polymers of methyl methacrylate (Bevington, Ghanem, and Melville, *loc. cit.*). When isotope dilution analyses were performed, the carrier and the reaction mixture were mixed in benzene solution before precipitation of the polymer. After the polymer had been filtered off, the filtrate was evaporated to dryness under a vacuum at low temperature; the solid residue was then purified by repeated crystallization.

The number-average molecular weights of polymers were determined by osmometry. The specific activities of radioactive materials were compared by the method of gas-counting; the materials were oxidised to carbon dioxide by wet oxidation. These assay procedures have been described fully (Bevington, Melville, and Taylor, *loc. cit.*). In the experimental results, the counting rates are directly proportional to the $^{14}C : {}^{12}C$ ratios in the samples being measured.

Certain samples of polystyrene were treated with trifluoroacetic anhydride and acetic acid. The polymer (about 300 mg.), trifluoroacetic anhydride (3 g.), glacial acetic acid (0·8 g.), and dry toluene (10 c.c.) were gently refluxed for 9 hr. The polymer was precipitated in the usual way in a large volume of cold methanol; the recovered polymer was dissolved in benzene and precipitated again in methanol.

Results.—*Separation tests.* It is essential that polymers prepared in the presence of labelled quinone or labelled initiator should be separated completely from uncombined active materials of low molecular weight. It has been shown that the technique of double precipitation removes almost every trace of uncombined initiator from polystyrene (Bevington, Melville, and Taylor, *loc. cit.*) and of uncombined *p*-benzoquinone from poly(methyl methacrylate) (Bevington, Ghanem, and Melville, *loc. cit.*). Tests on the separation of polystyrene from *p*-benzoquinone are now reported. In the first test, polystyrene was precipitated from benzene solution by using methanol containing dissolved [^{14}C]*p*-benzoquinone, and then the polymer was filtered off, washed, dried, and assayed; the polymer was redissolved in benzene, precipitated in pure methanol, washed, dried, and assayed. In the second test the inactive polymer and active quinone were mixed in benzene solution before precipitation in methanol. In both tests the ratio of the weight of quinone to the weight of polymer was greater than in any of the polymerization experiments. The tests are summarized in Table 1. The separation of polymer and quinone is clearly quite satisfactory.

TABLE 1.

|	Test 1	Test 2
Calc. Counts/min. : for no separation of polymer and quinone	1633	4660
Obs. after 1 pptn.	1·5	2
Obs. after 2 pptns.	0	2

Polymerizations with labelled initiator. The presence of *p*-benzoquinone caused the polymerization of styrene initiated by azo*iso*butyronitrile to be very slow in its early stages. The rate increased slightly with time but at one point there was quite a marked increase in rate to a value which was maintained at least as far as 5% conversion. Typical conversion–time plots are shown in the Figure. Evidently the quinone was not a complete inhibitor of the polymerization. Induction periods are recorded as the intercepts on the time axis of the linear parts of the conversion–time plots. The colour of the *p*-benzoquinone gradually disappeared during the induction period. The length of the induction period increased and the final steady rate decreased slightly as the initial concentration of quinone was raised.

Experiments with a fixed concentration of ^{14}C-initiator and various concentrations of unlabelled quinone are summarized in Table 2. These polymerizations were allowed to proceed to 5% conversion. The end-groups refer to $CMe_2 \cdot CN$ fragments from the initiator incorporated in the polymer.

A mixture of polymers 2, 3, and 4, having a counting rate of about 350 counts/min., was dissolved in chloroform and precipitated in diethyl ether which is a solvent for polystyrene of low molecular weight (Staudinger and Heuer, *Z. phys. Chem.*, 1934, *A*, **171**, 129). The precipitated polymer was redissolved in benzene and precipitated in methanol; 78% of the original polymer

was recovered. After drying, the recovered polymer had a counting rate of 213 counts/min.; if this polymer contains two initiator fragments per molecule, this activity corresponds to a molecular weight of 244,000.

Polymerizations with labelled benzoquinone. Experiments involving unlabelled initiator and [^{14}C]*p*-benzoquinone are summarized in Table 3. Expts. 6, 7, 8, and 9 were carried to 5% conversion. In expt. 10 the reaction was stopped after 1·93% conversion (calculated from
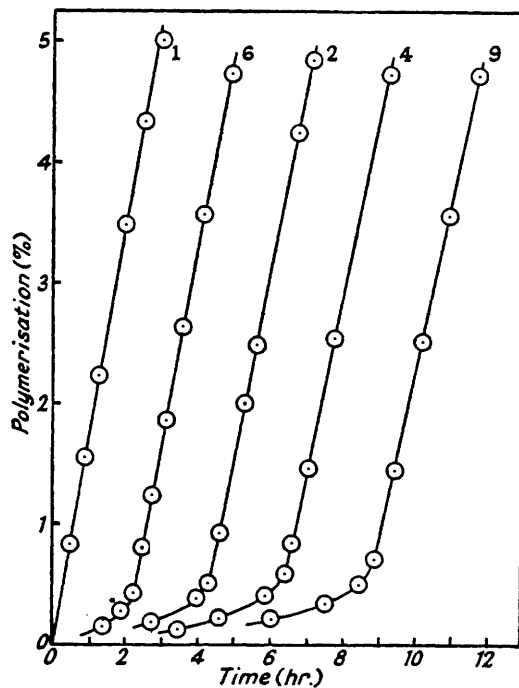
Conversion–time plots for typical experiments involving styrene, azoisobutyronitrile, and p-benzoquinone. (The numbering corresponds to that in Tables 2 and 3.)

the contraction); 0·25 g. of polymer was recovered whereas by calculation 0·30 g. should have been formed. In expt. 11, the calculated conversion was 0·86% but only about 77% of the calculated weight of polymer was recovered after precipitation in methanol, and its molecular weight was too low for osmometry. Assay of polymer no. 11 gave 700 counts/min. after 1

TABLE 2.

Expt. no.	Initiator concn. (g./l.)	Quinone concn. (g./l.)	Induction period (min.)	Steady rate (%/hr.)	M	counts/min. for polymer *	No. of end-groups per polymer mole
1	0·500	0	0	1·750	215,000	242	2·00
2	0·503	0·075	240	1·563	—	351	—
3	0·485	0·080	240	1·564	143,000	389	2·14
4	0·505	0·123	365	1·480	145,500	332	1·86
5	0·517	0·129	400	1·483	—	—	—

* counts/min. for initiator = 500,000.

TABLE 3.

Expt. no.	Initiator concn. (g./l.)	Quinone concn. (g./l.)	Induction period (min.)	Steady rate (%/hr.)	M	counts/min. polymer *	No. of quinone moles per polymer mole
6	0·500	0·050	120	1·698	143,000	29	0·53
7	0·503	0·055	150	1·624	150,000	28	0·54
8	0·514	0·101	380	1·566	142,500	49	0·90
9	0·493	0·157	505	1·460	153,500	86	1·70
10	0·486	0·119	—	—	63,000	227	1·85
11	0·503	0·121	—	—	—	561	—

* counts/min for *p*-benzoquinone = 99,400

precipitation and 561 counts/min. after 2 precipitations. The comparatively high rate shows that the polymer was quite rich in *p*-benzoquinone but the difference between the two values confirms that the molecular weight was low, since some of the smaller molecules were lost during the second precipitation. In Table 3 the numbers of *p*-benzoquinone molecules combined in each polymer are recorded.

A sample of polystyrene of average molecular weight near 150,000 and containing [^{14}C]-*p*-benzoquinone was precipitated in diethyl ether to remove material of comparatively low molecular weight, as described in a previous section. The counting rate was reduced from 35 to 6 counts/min., showing that the combined quinone was present in those polymer molecules which were of small size, and that in those molecules which were insoluble in ether there was little or no combined *p*-benzoquinone.

Experiments involving analyses. In order to see if the *p*-benzoquinone was completely consumed during the induction period, a reaction mixture containing [^{14}C]benzoquinone was made up and the quantity remaining at the end of the induction period was found by isotope dilution analysis. The original weight of the [^{14}C]quinone was 1·94 mg. and the weight of unlabelled quinone added as carrier was 415·6 mg.; the counting rate of the quinone after purification was 4 counts/min. The weight of [^{14}C]*p*-benzoquinone remaining in the mixture was therefore 0·017 mg., showing that less than 1% of the original material remained at the end of the induction period.

There may be direct reaction between *p*-benzoquinone and radicals formed by dissociation of the initiator, in which case the diether $C_6H_4(O \cdot CMe_2 \cdot CN)_2$ (I) should be found in the reaction mixture (Bickel and Waters, *loc. cit.*). The quantity of this material can be determined by isotope dilution analysis starting with either labelled quinone or labelled azo*iso*butyronitrile. In expt. 11, 3·3 mg. of [^{14}C]*p*-benzoquinone were used originally and 436·6 mg. of inactive diether (I) were added as carrier; the counting rate for the purified diether was 12 counts/min. The weight of (I) in the reaction mixture was therefore 0·123 mg., equivalent to 0·054 mg. of *p*-benzoquinone. Expt. 11 was interrupted at the end of the induction period so that all the quinone was consumed; thus 1·7% of the original quinone was converted into the diether. A similar analysis was performed in expt. 3 which involved ^{14}C-initiator and was allowed to proceed to 5% conversion. The weight of carrier was 280·3 mg. and the counting rate of the purified material was 58 counts/min.; the weight of (I) in the reaction mixture was therefore 0·057 mg., which corresponds to 2% of the *p*-benzoquinone present originally.

In expt. 12, a solution of azo[^{14}C]*iso*butyronitrile (13·62 mg.) and *p*-benzoquinone (4·37 mg.) in styrene (27·4 c.c.) was kept at 60° for 8½ hr. Isotope dilution analysis for tetramethyl-succinonitrile was performed; the weight of carrier was 555·3 mg. and the counting rate of the purified material was 480 counts/min. The weight of the dinitrile in the reaction mixture was therefore 0·534 mg.

Experiments involving trifluoroacetic anhydride. Polymer no. 9 (326·8 mg.) containing [^{14}C]*p*-benzoquinone was treated with trifluoroacetic anhydride and acetic acid as described in a previous section. After precipitation twice in methanol and drying, the counting rate of the polymer was 27 counts/min.; the counting rate for the original polymer was 86 counts/min. The combined filtrates from the precipitations were concentrated under reduced pressure and divided into two equal portions. To one portion pure quinol diacetate (349·6 mg.) was added; the solvent was removed under reduced pressure and the diacetate was purified by recrystallization; its counting rate was 11·5 counts/min. To the other portion, 2N-sodium hydroxide (80 c.c.) and pure quinol (634·8 mg.) were added; after refluxing for 30 min. the liquid was neutralized with hydrochloric acid. The liquid was distilled off under reduced pressure and from the residual solid a sample of pure quinol was prepared by repeated crystallization; its counting rate was 11 counts/min.

A sample of polystyrene with labelled CMe$_2$·CN end-groups, but completely free from *p*-benzoquinone, was treated with the trifluoroacetic anhydride reagent under the same conditions as in the experiment described above. The counting rate for the polymer was reduced from 234 to 209 counts/min.; the treatment did not cause the weight of polymer to increase.

DISCUSSION

General Features of the System.—In this paper *p*-benzoquinone is referred to as an inhibitor of the sensitized polymerization of styrene. The conversion–time plots in the Figure show, however, that polymerization is not completely inhibited in the so-called induction period. The transition from a slow reaction to a fast one is fairly abrupt and

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the character of the polymer produced during the slow reaction is very different from that of the polymer produced in the later stages, and the use of the term inhibitor is therefore justified; it must be recognised, however, that, compared with a material such as diphenyl-picrylhydrazyl, the quinone is inefficient as an inhibitor.

It was shown by isotope dilution analysis that less than 1% of the *p*-benzoquinone remained at the end of the induction period. It is believed that during the fast reaction the rate is that which would be expected if the quinone were absent; further, the molecular weight of the polymer produced after the induction period is the same as that of polymer formed in the complete absence of *p*-benzoquinone. The evidence for these views is now presented.

The steady rates observed after the induction periods are all slightly less than that in a normal polymerization (see Tables 2 and 3); the differences can be accounted for by consumption of initiator during the induction periods. The velocity constant for the decomposition of azo*iso*butyronitrile is known, and therefore the quantity of initiator remaining at the end of the induction period can be calculated. The observed rates can then be corrected to an initiator concentration of 0·500 g./l. by using the relation

$$\text{rate} \propto (\text{initiator concentration})^{\frac{1}{2}}$$

The velocity constant for the decomposition of the initiator is taken as $1 \cdot 20 \times 10^{-5}$ sec.$^{-1}$ at 60° (Bevington, *Trans. Faraday Soc.*, in the press). The corrected rates of polymerization are shown in Table 4.

TABLE 4.

Expt. no.	1	2	3	4	5	6	7	8	9
Initiator (%) remaining after induction period	100	84·2	84·2	77·1	75·3	91·7	90·0	83·0	69·8
Corrected rate (%/hr.)	1·75	1·65	1·69	1·68	1·68	1·77	1·70	1·70	1·76

There is little difference between the corrected rates, showing that in the main the differences between the rates observed in the various experiments were due to changes in initiator concentration. There is a tendency for the corrected rates in expts. 2—9 to be a little below that for expt. 1. This is to be expected, since the recorded induction periods are a little less than the times required for the steady rates of polymerization to be attained, and therefore the correcting factors are not quite large enough. It is clear also that during the induction period the quinone is not converted into substances which subsequently act as retarders.

Several observations show that the polymer produced during the induction period is of low molecular weight. Normally, the polymerizations were allowed to proceed to 5% conversion but in expts. 10 and 11 the reactions were stopped near the end of the induction period; in these cases the polymers were of low molecular weight and there was appreciable loss of polymer during precipitation. The experiments involving precipitation of polymers in diethyl ether, which is a solvent for polystyrene of molecular weight less than about 25,000, show that the polymers formed after the induction period contain no quinone and have a molecular weight by end-group analysis close to that of a polymer formed in a normal polymerization (the molecular weights are 244,000 and 215,000). In these experiments about 22% of the polymer remained in the ether solution. The unrecovered polymer is probably that formed during the induction period containing *p*-benzoquinone and having low molecular weight, but it is likely also to contain some of the polymer formed during the fast reaction; this would be the material at the low-molecular-weight end of the distribution. It is possible therefore to explain why the molecular weight of the material remaining after ether-extraction is a little greater than that of the normal polymer.

Ordinarily in polymers of styrene prepared at 60° by use of azo*iso*butyronitrile as initiator, there are two initiator fragments combined in each polymer molecule (Bevington, Melville, and Taylor, *J. Polymer Sci.*, 1954, **14**, 463). This shows that when polystyrene radicals interact they do so by combination. In both polymers 3 and 4, the number of initiator fragments per polymer is close to 2, even although these polymers contain appreciable numbers of molecules formed at early stages in the reactions. It is clear that almost all polymer radicals are destroyed by combination at all stages in the reaction.
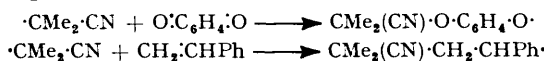
It is important to consider whether p-benzoquinone interferes in the initiation of poly-merization. The relative numbers of molecules of quinone and initiator consumed during the induction periods are given in Table 5. The last line of the Table gives the relative quantities of *available* radicals produced from the initiator during the induction periods; it must be noted that 1 mole of initiator gives 2 moles of radicals, and that, of the radicals

TABLE 5.

Expt. no.	2	3	4	5	6	7	8	9
Quinone consumed (moles)	6·94	7·41	11·39	11·95	4·63	5·09	9·35	14·54
Initiator decomposed (moles)	4·83	4·65	7·05	7·80	2·52	3·03	5·32	9·14
Available radicals produced (moles)	6·76	6·51	9·87	10·92	3·53	4·24	7·45	12·80

produced during the decomposition of the initiator, only about 70% are available for reaction with other substances (Bevington, *Nature*, 1955, **175**, 477) as shown by the fact that products of the interaction of initiator radicals are produced (see expt. 12). The rough agreement between the number of available radicals generated and the number of quinone molecules consumed does not indicate a direct reaction between the radicals and these molecules, since only small quantities of the products arising from such a reaction are found. Bickel and Waters (*loc. cit.*) showed that when 2-cyano-2-propyl radicals are generated in toluene solution in the presence of p-benzoquinone, the ethers (I) and $C_6H_4(OH)(O \cdot CMe_2 \cdot CN)$ (II) are formed; the yield of the former is about 4 times that of the latter, based on the quinone. Analyses for the ether (I) in expts. 3 and 11 showed that only about 2% of the quinone appeared as this product, and therefore about 90% of the quinone must have been incorporated in polymeric material. This shows clearly that the quinone exerts its effect by reacting with polymer radicals at an early stage in their growth rather than with the radicals formed directly by dissociation of the initiator. Cohen (*J. Polymer Sci.*, 1947, **2**, 511) also presented evidence leading to this conclusion.

It is possible to compare the velocity constants for the alternative reactions

$$\cdot CMe_2 \cdot CN + O \dot{:} C_6H_4 \dot{:} O \longrightarrow CMe_2(CN) \cdot O \cdot C_6H_4 \cdot O \cdot$$
$$\cdot CMe_2 \cdot CN + CH_2 \dot{:} CHPh \longrightarrow CMe_2(CN) \cdot CH_2 \cdot CHPh \cdot$$

Consider experiment 3. Analysis for the ether (I) showed that 2% of the quinone appeared as this product; it is probable therefore that about 8% was converted into (II). The relative figures in Table 5 being used, these quantities of quinone are equivalent to 0·15 mole and 0·30 mole of azo-compound respectively. About 10% of the initiator decomposing during the induction period appeared therefore as products not containing styrene; a further 30% of the decomposed initiator reacted with neither quinone nor monomer; the remaining 60% must have reacted with styrene. The concentration of styrene was near 8·5 moles/l. and the average concentration of quinone during the induction period was about 4×10^{-4} mole/l. Putting

$$\frac{\text{Rate of reaction of radicals with quinone}}{\text{Rate of reaction of radicals with monomer}} = \frac{k_x[R][Q]}{k_i[R][M]} = \frac{10}{60}$$

where $[R]$, $[Q]$, and $[M]$ are the concentrations of radicals, quinone, and monomer respectively, we find k_x/k_i to be about 3500.

Structures of Polymers containing p-*Benzoquinone.*—Mechanisms by which p-benzoquinone might react with polymer radicals have been summarized by Flory ("Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, New York, 1953, p. 164). Bickel and Waters (*loc. cit.*) showed that the radical $\cdot CMe_2X$, where X is CN or CO_2CH_3, attacks p-benzoquinone at the oxygen atom giving $CXMe_2 \cdot O \cdot C_6H_4 \cdot O \cdot$ as the first product; they found no evidence for the occurrence of nuclear substitution in the quinone. The radicals studied by Bickel and Waters have reactivities similar to those present in polymerizing styrene or methyl methacrylate, and it is likely therefore that polystyrene containing com-bined p-benzoquinone can be represented as $RO \cdot C_6H_4 \cdot OR$.

The results of the preliminary experiments involving trifluoroacetic anhydride are also consistent with the belief that the quinone is bound into the polymer by two ether linkages. There is evidence that the trifluoroacetic anhydride reagent causes the cleavage of ether

linkages (Bourne, Burdon, and Tatlow, personal communication). A polymer containing [^{14}C]p-benzoquinone and having the formula shown above should lose its activity if treated with the reagent, and in fact the specific activity of polystyrene no. 9 was reduced to less than one-third of its original value. A complicating factor is that the introduction of acetyl groups into certain aromatic substances can be promoted by trifluoroacetic anhydride (Bourne, Randles, Stacey, Tatlow, and Tedder, *J. Amer. Chem. Soc.*, 1954, **76**, 3206). The reduction of the specific activity of polymer no. 9 might therefore be due in part to the addition of non-radioactive carbon atoms to the polymer molecules. If this effect were the sole reason for the reduction in activity, it would imply that 8 acetyl groups become attached to each monomer unit, which is most improbable. Further, the control experiment with polystyrene containing labelled end-groups but no quinone showed that the introduction of acetyl groups is comparatively unimportant.

It is believed (Bourne, Randles, *et al.*, *loc. cit.*) that in a mixture of trifluoroacetic anhydride and acetic acid, the mixed anhydride $CF_3 \cdot CO \cdot O \cdot CO \cdot CH_3$ and the ions $CH_3 \cdot CO^+$ and $CF_3 \cdot CO \cdot O^-$ are formed. The cation may attack an ether linkage in the polymer to form an oxonium ion thus :
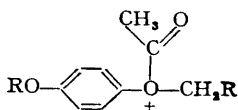
This oxonium ion may break down to give $RO \cdot C_6H_4 \cdot O \cdot CO \cdot CH_3$ and $R \cdot CH_2 \cdot O \cdot CO \cdot CF_3$ (by reaction of the other fragment with $CF_3 \cdot CO \cdot O^-$) or alternatively it might break down to $RO \cdot C_6H_4 \cdot O \cdot CO \cdot CF_3$ and $R \cdot CH_2 \cdot O \cdot CO \cdot CH_3$. As a result of the cleavage with trifluoroacetic anhydride and acetic acid, the p-benzoquinone which is split out of the polymer may be present in three forms, *viz.*, p-$CH_3 \cdot CO \cdot O \cdot C_6H_4 \cdot O \cdot CO \cdot CH_3$ (III), p-$CH_3 \cdot CO \cdot O \cdot C_6H_4 \cdot O \cdot CO \cdot CF_3$ (IV), and p-$CF_3 \cdot CO \cdot O \cdot C_6H_4 \cdot O \cdot CO \cdot CF_3$ (V). Isotope dilution analysis revealed the presence of 0·134 mg. of diacetate (III), equivalent to 0·075 mg. of p-benzoquinone. Quinol would be formed from all three esters on hydrolysis; analysis showed that 0·140 mg. of quinol was produced, equivalent to 0·137 mg. of p-benzoquinone. If the reduction in the specific activity of the polymer were due solely to the removal of p-benzoquinone, the weight of quinone cleaved out of the polymer must have been 0·268 mg.   The discrepancy between the two weights of quinone can be explained by the introduction of acetyl groups into the benzene rings of the polymer.   Some of the acetyl groups might be substituted in the benzene rings of the styrene units, and some might be situated in the benzene rings of the esters (III), (IV), and (V).   Substitution in the styrene units was discussed above; if acetyl groups had been introduced into the esters, the resulting compounds would not have shown up in the analyses for the quinol and its diacetate.

It is concluded that the experiments involving trifluoroacetic anhydride show that some at least of the p-benzoquinone is incorporated in polystyrene by ether linkages. The quinone thus bound can be split out by means of trifluoroacetic anhydride and acetic acid; one of the products is quinol diacetate, but esters of quinol containing fluorine are also formed.

Comparison of Methyl Methacrylate and Styrene.—Comparison of the effects of p-benzo-quinone upon the sensitized polymerizations of styrene and methyl methacrylate shows that the addition of a molecule of the quinone to the polymer radical occurs more readily for styrene than for methyl methacrylate. The interaction between a polymer radical and a molecule of p-benzoquinone is represented as

(1)   R· + O=⟨ ⟩=O ⟶ R—O—⟨ ⟩—O· ;   velocity constant $= k_r$
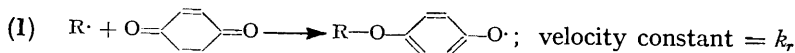
and the propagation reaction as

(2)   R· + M ⟶ R — M· ;   velocity constant $= k_p$
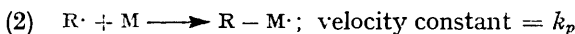
Thus

$$\frac{\text{Rate of reaction (1)}}{\text{Rate of reaction (2)}} = \frac{k_r[R][Q]}{k_p[R][M]} = \frac{k_r[Q]}{k_p[M]}$$

where [R], [Q], and [M] are as defined on p. 2827. For the retarded polymerization of methyl methacrylate and the slow polymerization of styrene, [Q] and [M] are about equal. The difference between the two systems can be expressed as

$$(k_r/k_p) \text{ styrene} > (k_r/k_p) \text{ methyl methacrylate}$$

The values of these ratios can be estimated as follows. Consider expt. 3. During the induction period about 0·8% of the monomer polymerized and all the quinone was consumed; considering 1 l. of reaction mixture, 0·07 mole of styrene and $7·5 \times 10^{-4}$ mole of p-benzoquinone were incorporated in polymer. The ratio k_r/k_p can be calculated in the same way as the ratio k_r/k_i, and it is found to be 227; there is therefore a marked difference between these ratios. In an experiment with methyl methacrylate, *viz.*, expt. no. 20 in the paper by Bevington, Ghanem, and Melville (*loc. cit.*), 1 molecule of quinone was combined with 1305 molecules of methyl methacrylate; in this experiment the average concentration of quinone can be taken as $1·5 \times 10^{-3}$ mole/l. (*i.e.*, not very different from its initial value) and the concentration of monomer as 9 moles/l. The value of k_r/k_p for methyl methacrylate is therefore about 4·5. The value at 60° for k_p for methyl methacrylate is about three times that for styrene, and therefore k_r for styrene is 16 times k_r for methyl methacrylate. This implies that the styrene radical is more reactive than the methyl methacrylate radical towards p-benzoquinone; study of co-polymerizing systems indicates that generally the methyl methacrylate radical is a little more reactive than the styrene radical.

It was shown (Bevington, Ghanem, and Melville, *loc. cit.*) that the radical $RO \cdot C_6H_4 \cdot O \cdot$, where R represents a poly(methyl methacrylate) chain, is comparatively unreactive. This ether radical has only a slight tendency to attack a molecule of monomer to give the new radical $RO \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CMe \cdot (CO_2Me) \cdot$ which is able to engage in further growth reactions; the ether radical usually combines with an ordinary poly(methyl methacrylate) radical to give the molecule $RO \cdot C_6H_4 \cdot OR$. The ether radical formed by the attack of a polystyrene radical on p-benzoquinone is able to add on a molecule of styrene rather more readily; this is shown by the fact that polymers formed during the induction periods contain on the average nearly two molecules of the quinone per polymer molecule. There is therefore a slight tendency for the quinone to co-polymerize with styrene. The conclusion that there is a greater tendency for p-benzoquinone to co-polymerize with styrene than with methyl methacrylate is in agreement with the accepted view that the styrene molecule is a little more reactive than the methyl methacrylate molecule.

The combination $2 RO \cdot C_6H_4 \cdot O \cdot \longrightarrow RO \cdot C_6H_4 \cdot O \cdot O \cdot C_6H_4 \cdot OR$ would lead to the inclusion of two quinone molecules in each polymer molecule; this combination seems rather unlikely, however, since the product is a peroxide. The most likely termination reaction in the early stages of the polymerization can be represented as $X \cdot R \cdot O \cdot C_6H_4 \cdot O \cdot + \cdot R'O \cdot C_6H_4 \cdot OR'' \cdot X \longrightarrow X \cdot R \cdot O \cdot C_6H_4 \cdot O \cdot R' \cdot O \cdot C_6H_4 \cdot O \cdot R'' \cdot X$ where R, R', and R'' represent short polystyrene chains, and X represents an initiator fragment.

Conclusion.—The results in this paper show that the use of reagents labelled with ^{14}C can provide most valuable information about the mechanisms of complex organic reactions. Results can be obtained by using labelled reagents of quite moderate specific activity. It has been possible to determine accurately products of low molecular weight formed simultaneously with polymer even if the weights of these products are very considerably less than 1 mg. and the substances are present in complex mixtures. In investigating polymerizing systems, it is necessary to combine the isotopic methods with older methods of study, *e.g.*, determination of rates of reaction and of average molecular weights of polymers, in order to obtain a complete picture of the reaction.

It has been shown that when styrene is polymerized in the presence of p-benzoquinone, growth of the polymer radicals is stopped prematurely by interaction with the quinone. Most of the quinone becomes incorporated in polymer, but some of it reacts with radicals generated from the initiator to give products of low molecular weight. There is clear evidence that there is limited co-polymerization of styrene and p-benzoquinone. When the quinone is all consumed, the rate of polymerization rises to its normal value, and the

polymer then produced has the same molecular weight as a polymer prepared in the complete absence of p-benzoquinone with use of the same concentration of initiator. Additional evidence has been obtained that polymer radicals attack the molecule of p-benzoquinone at the oxygen atoms. It is shown that the use of labelled substances may assist materially in elucidating the mechanisms of reactions involving new organic reagents, *e.g.*, trifluoro-acetic anhydride.